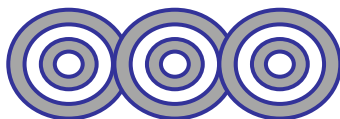




# Instrumental Methods of Analysis



## An Introduction to Electrochemical Methods

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# **Overview of Electrochemistry**

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Electrochemistry is the branch of chemistry concerned with the interrelation of **electrical** and **chemical** effects.

A large part of this field deals with the study of;

- Chemical changes caused by the passage of an electric current and

- The production of electrical energy by chemical reactions.

Analytical methods in which a measurement of **potential**, **current**, or **charge** in an electrochemical cell serves as the analytical signal.

## Oxidation/reduction reaction

In an oxidation/reduction reaction (**redox reactions**) electrons are transferred from one reactant to another.

An example is the oxidation of iron(II) ions by cerium(IV) ions. The reaction is described by the equation:



In this reaction, an electron is transferred from  $\text{Fe}^{2+}$  to  $\text{Ce}^{4+}$  to form  $\text{Ce}^{3+}$  and  $\text{Fe}^{3+}$  ions.

A substance that has a strong affinity for electrons, such as  $\text{Ce}^{4+}$ , is called an **oxidizing agent**, or an **oxidant**. A **reducing agent**, or **reductant**, is a species, such as  $\text{Fe}^{2+}$ , that donates electrons to another species.

we can say that

- **Fe<sup>2+</sup>** is oxidized by **Ce<sup>4+</sup>**,
- similarly,
- **Ce<sup>4+</sup>** is reduced by **Fe<sup>2+</sup>**.



We can split any oxidation/reduction equation into two half-reactions that show which species gains electrons and which loses them.

For example, Equation above is the sum of the two half-reactions:



In a way that is analogous to the Bronsted-Lowry concept of acid/base reactions, when an acid donates a proton, it becomes a conjugate base that is capable of accepting a proton.



By analogy, when a reducing agent donates an electron, it becomes an oxidizing agent that can then accept an electron. This product could be called a conjugate oxidant, (but that terminology is seldom). With this idea in mind, we can write a generalized equation for a redox reaction as



In this equation,  $B_{\text{ox}}$ , the oxidized form of species B, accepts electrons from  $A_{\text{red}}$  to form the new reductant,  $B_{\text{red}}$ . At the same time, reductant  $A_{\text{red}}$ , having given up electrons, becomes an oxidizing agent,  $A_{\text{ox}}$ .

If we know from chemical evidence that the equilibrium in Equation lies to the right, we can state that  $B_{\text{ox}}$  is a better electron acceptor (stronger oxidant) than  $A_{\text{ox}}$ . Likewise,  $A_{\text{red}}$  is a more effective electron donor (better reductant) than  $B_{\text{red}}$ .

## EXAMPLE

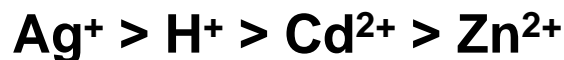
The following reactions are spontaneous and thus proceed to the right, as written:



What can we deduce regarding the strengths of  $\text{H}^+$ ,  $\text{Ag}^+$ ,  $\text{Cd}^{2+}$ , and  $\text{Zn}^{2+}$  as electron acceptors (or oxidizing agents)?

## Solution

The second reaction establishes that  $\text{Ag}^+$  is a more effective electron acceptor than  $\text{H}^+$ ; the first reaction demonstrates that  $\text{H}^+$  is more effective than  $\text{Cd}^{2+}$ . Finally, the third equation shows that  $\text{Cd}^{2+}$  is more effective than  $\text{Zn}^{2+}$ . Thus, the order of oxidizing strength is



# Oxidation/Reduction Reactions in Electrochemical Cells

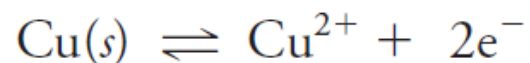
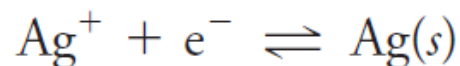
Many oxidation/reduction reactions can be carried out in either of two ways that are physically quite different.

-In one, the reaction is performed by bringing the oxidant and the reductant into **direct contact** in a suitable container.

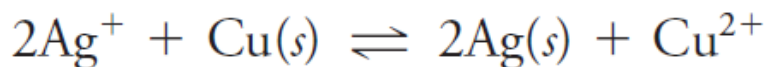
-In the second, the reaction is carried out in an **electrochemical cell** in which the reactants do not come in direct contact with one another.



A spectacular example of direct contact is the famous experiment in which a piece of copper Cu is immersed in a silver nitrate  $\text{AgNO}_3$  solution. Silver ions migrate to the metal and are reduced:



By multiplying the silver half-reaction by two and adding the reactions, we obtain a net ionic equation for the overall process:



Immersing a piece of copper in a solution of silver nitrate. The result is the deposition of silver on the copper in the form of a “silver-tree.”

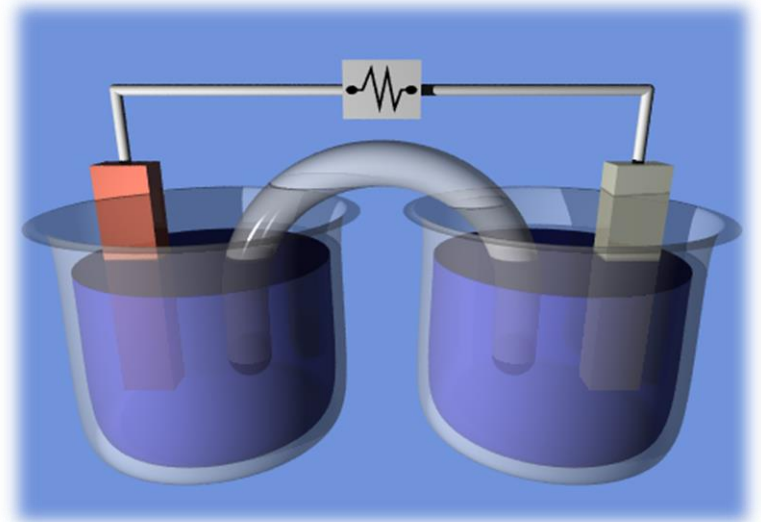


Photograph of a “silver tree” created by immersing a coil of copper wire in a solution of silver nitrate.

## Electrochemical Cell

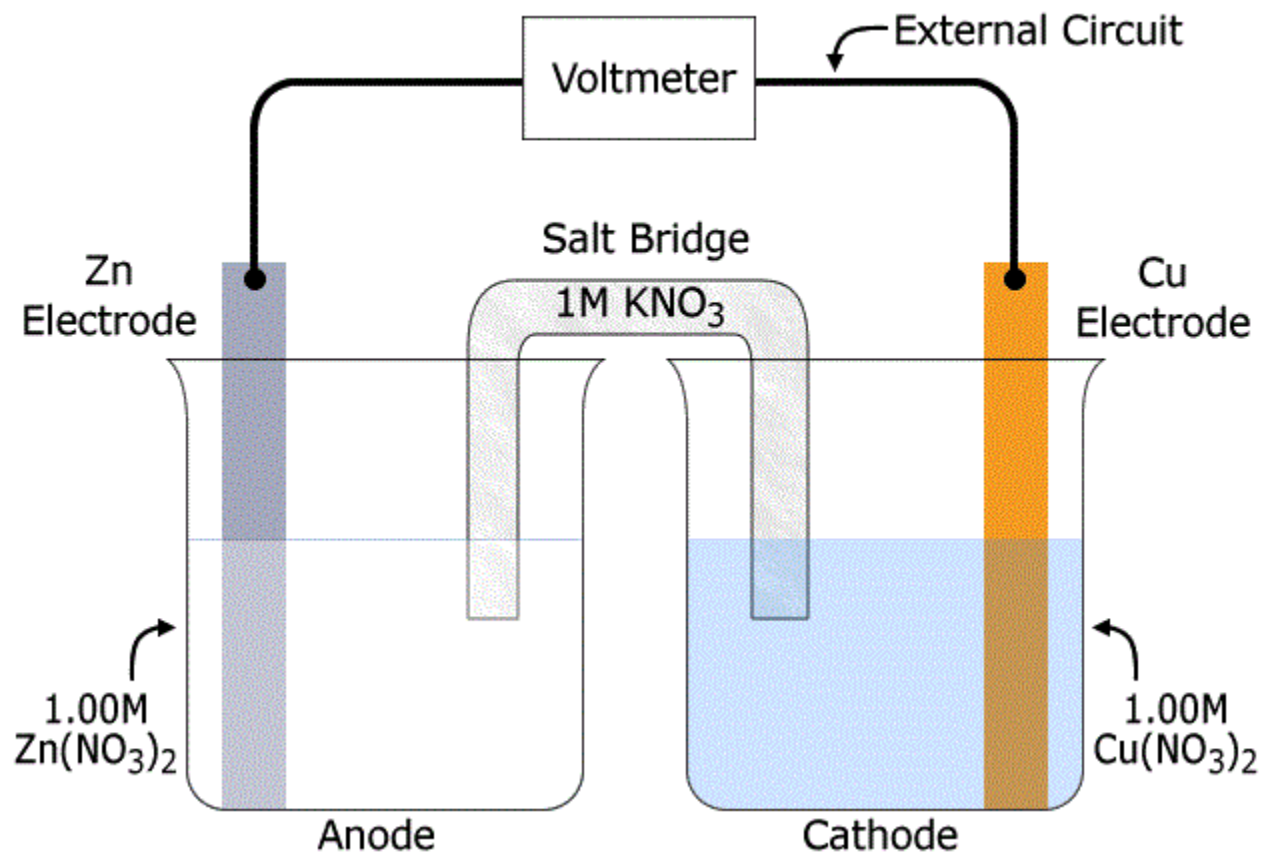
Electrochemical measurements are made in an electrochemical cell, An **electrochemical cell** is a device capable of either generating electrical energy from chemical reactions or facilitating chemical reactions through the introduction of electrical energy.

Electrochemical cell consists of two or more conductors called **electrodes**, and associated electronics for controlling and measuring the current and potential. Each electrode immersed in a suitable **electrolyte solution**.



For a current to develop in a cell, it is necessary

- (1) That the electrodes be connected externally by means of a metal conductor and
- (2) That the two electrolyte solutions be in contact to permit movement of ions from one to the other.



Typical electrochemical cell consists of zinc electrode immersed in a solution of zinc nitrate, and a copper electrode in a solution of copper nitrate. The two solutions are joined by a **salt bridge**, which consists of a tube filled with a solution that is saturated with potassium nitrate or some other electrolyte.

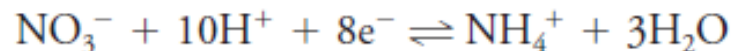
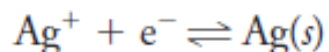
The purpose of the salt bridge is to isolate the contents (prevent direct reaction) of the two halves of the cell while maintaining electrical contact between them.

# Cathodes and Anodes

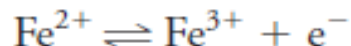
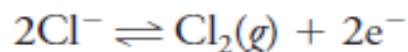
The **cathode** in an electrochemical cell is the electrode at which reduction occurs (accept electrons).

The **anode** in an electrochemical cell is the electrode at which an oxidation takes place (donate electrons).

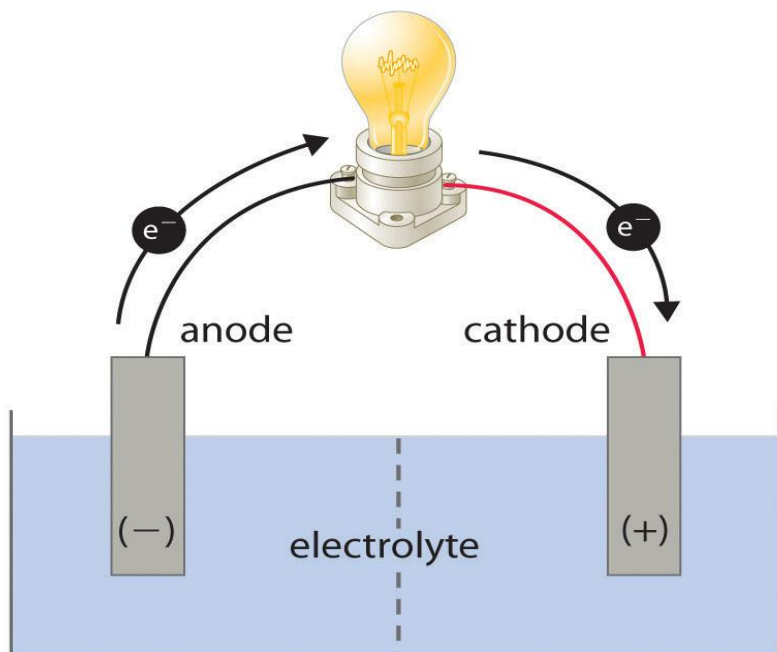
Examples of typical cathodic reactions include:



Examples of typical anodic reactions include:



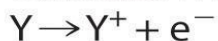
# Types of Electrochemical Cells



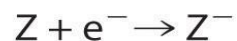
**GALVANIC CELL**

Energy released by spontaneous redox reaction is converted to electrical energy.

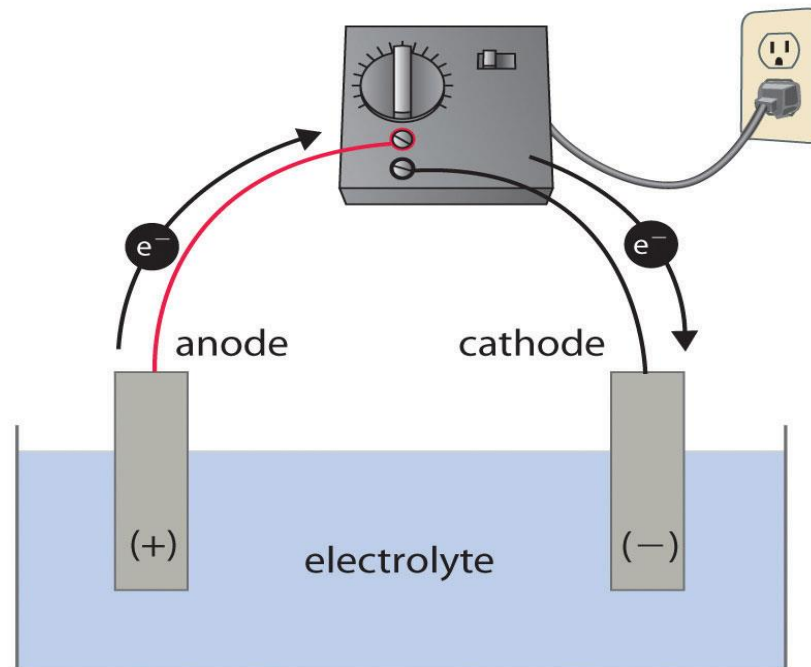
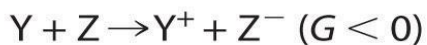
Oxidation half-reaction:



Reduction half-reaction:



Overall cell reaction:



**ELECTROLYTIC CELL**

Electrical energy is used to drive nonspontaneous redox reaction.

Oxidation half-reaction:



Reduction half-reaction:



Overall cell reaction:



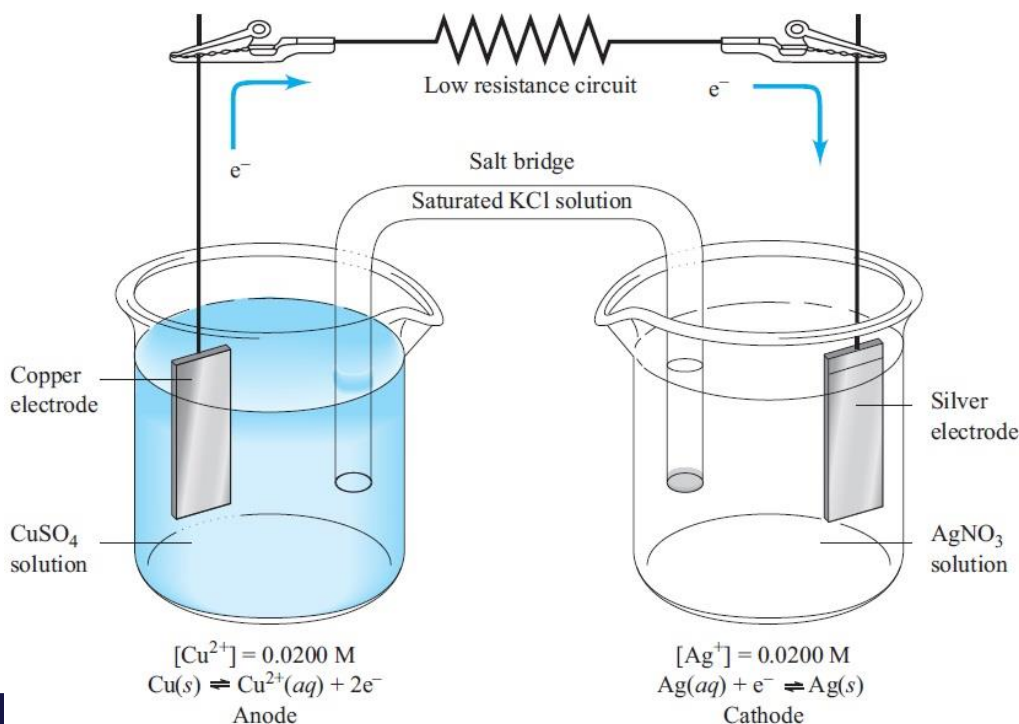
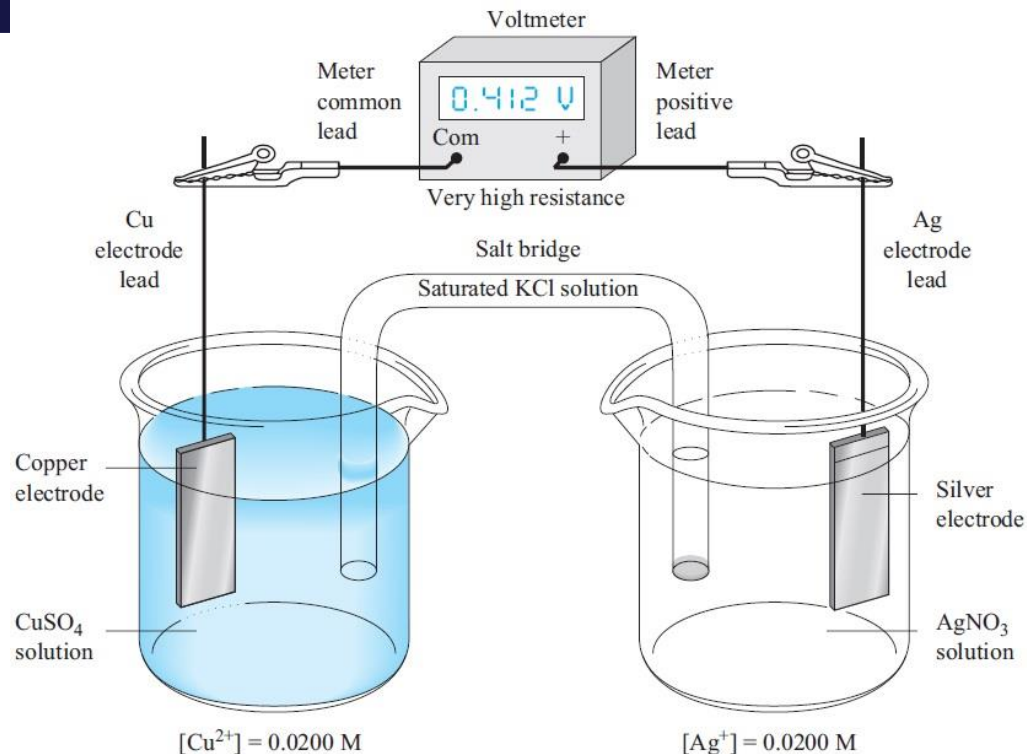
Electrochemical cells are either **galvanic** or **electrolytic**.

**Galvanic**, or **voltaic**, **cells** store electrical energy. The reactions at the two electrodes in such cells tend to proceed **spontaneously** and produce a flow of electrons from the anode to the cathode via an external conductor. Galvanic cells operate spontaneously, and the net reaction during discharge is called the spontaneous cell reaction.

An **electrolytic cell**, in contrast, requires an external source of electrical energy for operation (consume electrical energy). External current supplied to drive **nonspontaneous** redox reaction. Note that in the electrolytic cell, the direction of the current is the reverse of that in the galvanic cell.

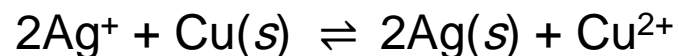
## Galvanic cell (example)

A galvanic cell that exhibits a potential of about 0.412 V when no current is being drawn from it. The silver electrode is +ve with respect to the copper electrode in this cell. The copper electrode, which is -ve with respect to the silver electrode, is a potential source of electrons to the external circuit when the cell is discharged.



The same cell, but now it is under discharge so that electrons move through the external circuit from the copper electrode to the silver electrode. While being discharged, the silver electrode is the cathode since the reduction of  $\text{Ag}^+$  occurs here. The copper electrode is the anode since the oxidation of  $\text{Cu}(s)$  occurs at this electrode.

The net reaction (spontaneous cell reaction):

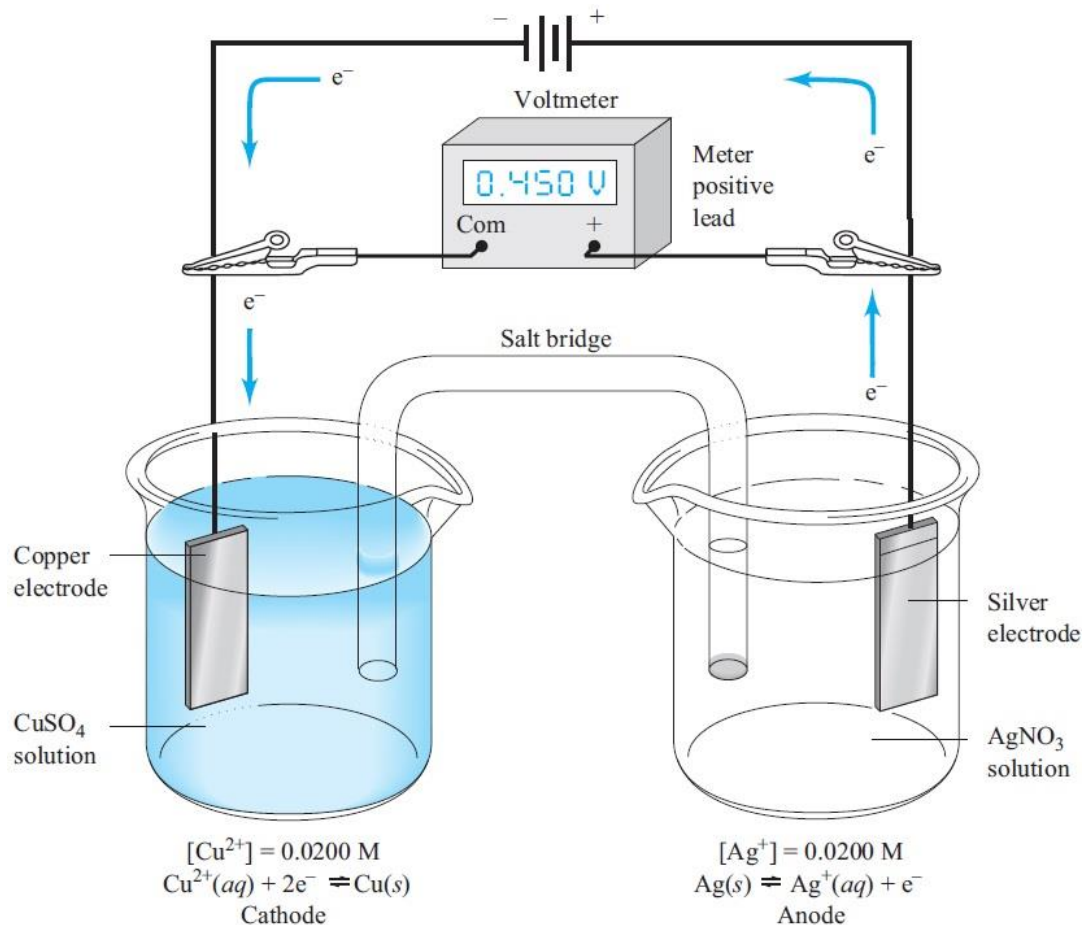
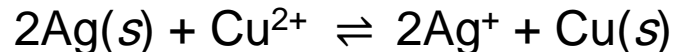


## Electrolytic cell (example)

The galvanic cells can be operated as an electrolytic cell by connecting the +ve terminal of an external voltage source with a potential somewhat greater than that produced by that galvanic cell to the cathodic electrode and the -ve terminal of the source to the anodic electrode.

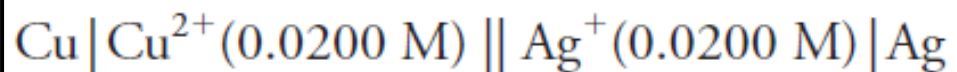
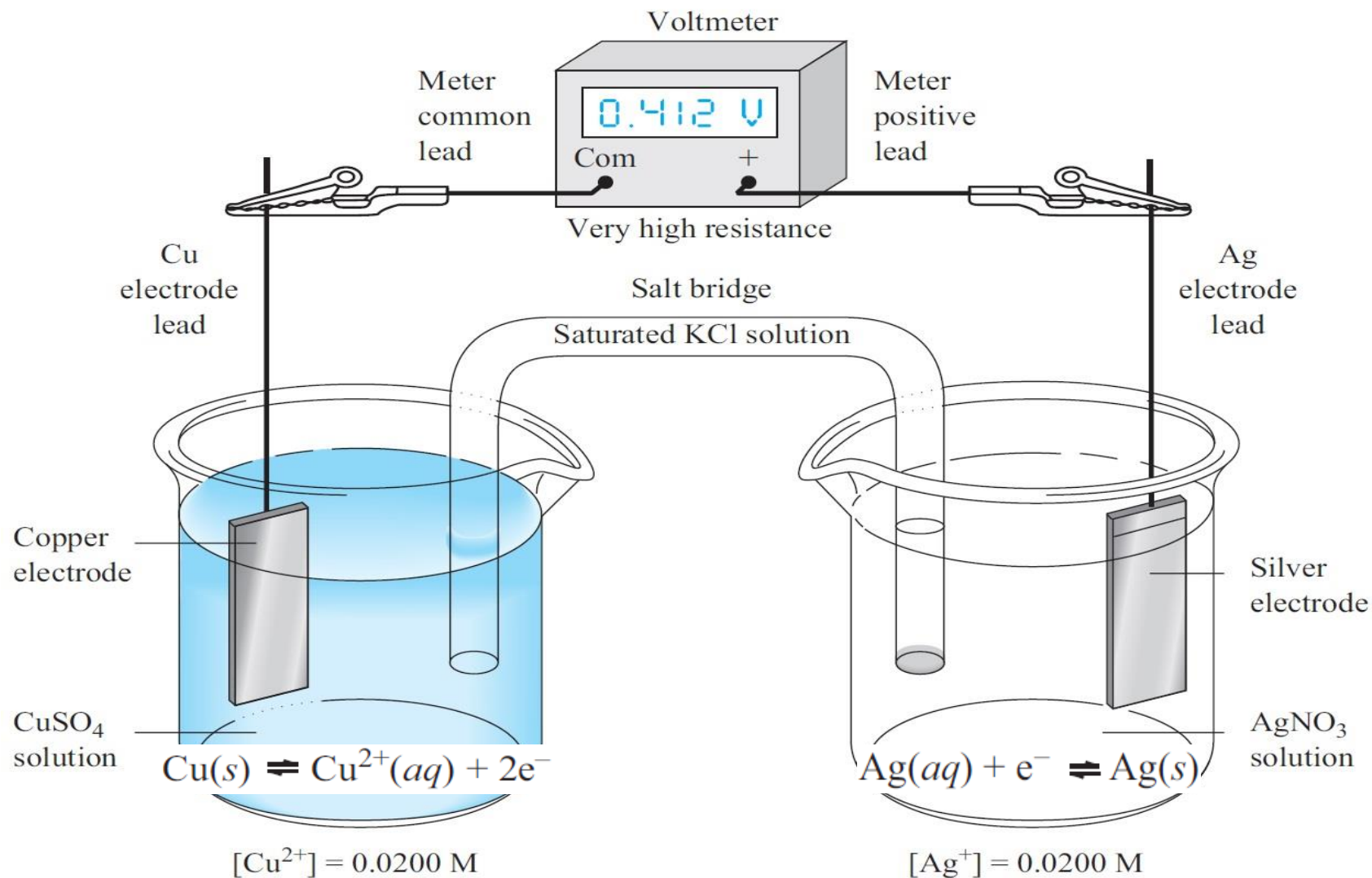
Electrons flow from the -ve terminal of the external voltage source to the copper electrode, where reduction of  $\text{Cu}^{2+}$  to  $\text{Cu(s)}$  occurs. The current is sustained by the oxidation of  $\text{Ag(s)}$  to  $\text{Ag}^+$  at the right-hand electrode, producing electrons that flow to the +ve terminal of the voltage source. In the electrolytic cell, the direction of the current and the reactions at the electrodes are reverse of that in the galvanic cell. The silver electrode is forced to become anode, while the copper electrode is forced to become cathode.

The net reaction is the opposite of the galvanic cell:





# Representing Cells Schematically



# Movement of charge in a galvanic cell

