

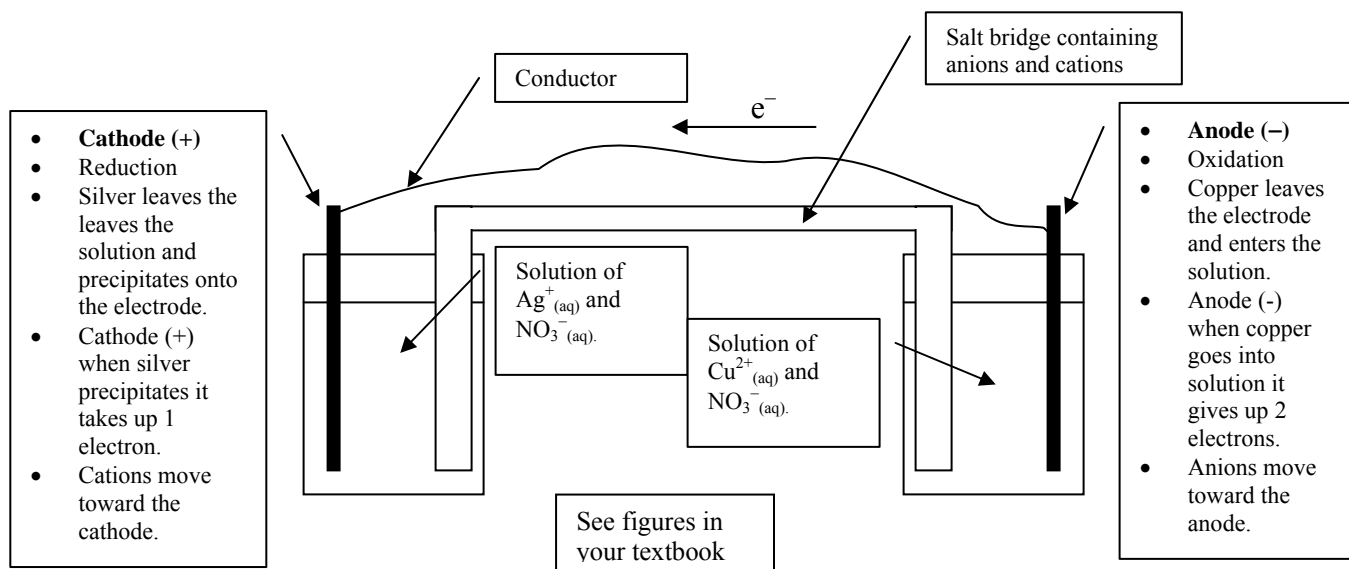
9.5 Galvanic Cells

- Electric cells adapted for scientific study are often called galvanic cells (Luigi Galvani) or voltaic cells (Alessandro Volta).
- In a cell a trick is played on the oxidizing and reducing agents, the electrons forced to travel through an external circuit.
- In order to study an electric cell, scientists have modified the basic cell into half-cells. See figure 1 on page 695.
- Of the two primary types of half-cells, the first uses a salt bridge and the other uses a porous cup to keep the electrolytes separated.
- Half-cell: an electrode and an electrolyte forming half a complete cell.
- Cell notation example: $\text{Cu}_{(s)} \mid \text{Cu}(\text{NO}_3)_{2(aq)} \parallel \text{Zn}(\text{NO}_3)_{2(aq)} \mid \text{Zn}_{(s)}$
 \mid = phase boundary between electrode and electrolyte
 \parallel = physical boundary between half cells
half-cell 1 = copper electrode in copper nitrate solution
half-cell 2 = zinc electrode in zinc nitrate solution

cathode (+) \mid electrolyte \parallel electrolyte \mid anode (–)
reduction oxidation
anions \rightarrow \leftarrow cations

A Theoretical Description of a Galvanic Cell

- Galvanic cell: an arrangement of two half-cells that can produce electricity spontaneously.
- The strongest oxidizing agent present in the cell always undergoes a reduction at the cathode.
- The strongest reducing agent present in the cell always undergoes an oxidation at the anode.
- Cathode: the electrode where reduction occurs
- Anode: the electrode where oxidation occurs.
- E.g. $\text{Ag}_{(s)} \mid \text{AgNO}_{3(aq)} \parallel \text{Cu}(\text{NO}_3)_{2(aq)} \mid \text{Cu}_{(s)}$



- In an electric cell or battery, the cathode is the positive electrode and the anode is the negative electrode.
- Electricity flows from the anode through an external conductor (wire) to the cathode.

- From the example above:
 - Silver is the strongest oxidizing agent and undergoes reduction at the cathode.
 - Copper is the strongest reducing agent and undergoes oxidation at the anode.
 - Electrons released by oxidation at the anode flow to the cathode for reduction through an external circuit.
 - As the silver is precipitated the positive charge decreases and there is a flow of cations through the salt bridge to the cathode side of the cell to keep the cell neutral.
 - As the copper enters solution the positive charge increases in there is a flow of anions through the salt bridge to the anode side of the cell to keep the cell neutral.

Galvanic Cells with Inert Electrodes

- In the example above the half-cell contains a metal and a salt of the metal. What if the electrolyte cannot form a solid to act as an electrode. E.g. Dichromate is an ionic substance and an electrode made of dichromate would dissolve in the electrolyte.
- An inert electrode can be used when a suitable electrode is not available.
- Inert electrode: a solid conductor that will not react with any substances present in a cell (usually carbon or platinum).
- See figure 1 and example on page 699.
 - In the example the copper oxidizes and enters the solution and generates electrons.
 - The anode side becomes darker blue as copper is dissolved.
 - The carbon does not react with the dichromate and remains unchanged. Some of the dichromate ions migrate to the anode. The dichromate is reduced to chromium.
 - The carbon only gives a surface for electron transfer and a place for the reaction to occur.

Standard Cells and Cell Potentials

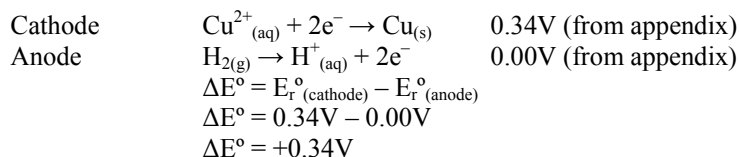
- Standard Cell: a galvanic cell in which each half-cell contains all entities shown in the half-reaction equation at SATP conditions, with concentrations of 1.0 mol/L for the aqueous entities.
- Standard Cell Potential: ΔE° is the maximum electric potential difference (voltage) of a cell operating under standard conditions.
- Standard Reduction Potential: E_r° represents the ability of a standard half-cell to attract electrons in a reduction half-reaction.
- Reference Half-Cell: a half-cell arbitrarily assigned an electrode potential of exactly zero volts; the standard hydrogen half-cell.
- $\Delta E^\circ = E_r^\circ(\text{cathode}) - E_r^\circ(\text{anode})$
- It is impossible to determine the reduction potential of a single half-cell since both an oxidizing and reducing agent are needed. Therefore all half-cells are determined using the experimental half-cell and the arbitrary zero half-cell (the hydrogen half-cell). You need 2 half-cells to determine a difference (ΔE°).

Standard Hydrogen Half-Cell

- The standard hydrogen half-cell consists of an inert platinum electrode immersed in a 1.00 mol/L solution of hydrogen ions, with hydrogen gas at a pressure of 100 kPa bubbling over the electrode at SATP.
- $2\text{H}^+_{(\text{aq})} + 2\text{e}^- \rightarrow \text{H}_{2(\text{g})}$ $E_r^\circ = 0.00\text{V}$
- A positive reduction potential means that the electrons are drawn away from the hydrogen half-cell.
- A negative reduction potential means that the electrons are drawn toward the hydrogen half-cell.
- See figure 6 on page 702.

Measuring Standard Reduction Potentials

- The standard reduction potential of a half-cell can be measured by constructing a standard cell using a hydrogen reference half-cell and the half-cell whose reduction potential you want to measure.
- E.g. $\text{Cu}_{(\text{s})} \mid \text{Cu}^{2+}_{(\text{aq})} \parallel \text{H}_{2(\text{g})}, \text{H}^+_{(\text{aq})} \mid \text{Pt}_{(\text{s})}$ $\Delta E^\circ = +0.34\text{V}$



- A positive cell potential (ΔE°) indicates that the net reaction is spontaneous – a requirement for all galvanic cells.

Cell Potentials Under Nonstandard Conditions

- As a cell operates it loses material. To determine the cell potential use the Walther Hermann Nernst equation.

- $\Delta E = \Delta E^\circ - \frac{0.0592\text{V}}{n} \log Q$, at 25°C only

where

ΔE = is the cell potential at 25°C at non-standard concentrations

ΔE° = is the cell potential at 25°C at standard concentrations

n = number of moles of electrons transferred according to the cell reaction

Q = the reaction quotient