

ELECTROCHEMICAL CELLS

A redox reaction involves the transfer of electrons from one chemical species to another. The energy from a redox reaction can be used to accomplish work by constructing an electrochemical cell. In an electrochemical cell, the oxidation process and the reduction process are separated into two **half-cells** connected by an external wire. The half-cell with the oxidation process is losing negative charge (e⁻ loss) while the half-cell with the reduction process is gaining negative charge (e⁻ gain). To maintain electrical neutrality in both half-cells, a salt bridge (or semipermeable membrane) must connect the two half-cells to permit the transfer of ions between the two solutions. Thus, the salt bridge completes the electrical circuit between the half cells.

The transfer of electrons through the external wire create a current that can do work. The driving force pushing the electrons through the wire is the difference in the attraction for electrons in the two half-cells. This voltage difference is called the **cell potential (E_{cell})** and is measured in volts. The cell potential (E_{cell}) is directly related to the magnitude of the equilibrium constant for the overall oxidation-reduction reaction occurring in the cell. A reaction that more strongly favors product formation (larger K_{eq}) will have a higher cell potential (larger E_{cell}) than a reaction which only moderately favors product formation.

Standard cell potentials (E^o_{cell}) can be calculated from potentials (E^o) for oxidation and reductions reactions measured under standard conditions (1.00 M solutions, 1.00 atm pressure, 298 K). A positive cell potential means the reaction proceeds spontaneously in the direction the reaction is written; a reaction with a negative cell potential proceeds spontaneously in the reverse direction.

$$(1) \quad E^{\circ}_{\text{cell}} = E^{\circ}_{\text{reduction}} + E^{\circ}_{\text{oxidation}}$$

When the concentrations of solutes or partial pressures of gases are **not** at standard conditions, the cell potential (E_{cell}) can be determined with the **Nernst equation (2)**:

$$(2) \quad E_{\text{cell}} = E^{\circ}_{\text{cell}} - (0.059 / n) \log Q \quad (\text{Nernst equation})$$

Q: reaction quotient

n: moles of e⁻ transferred

For the general cell reaction (3) occurring at 298 K, the Nernst equation can be rewritten as shown in (4):

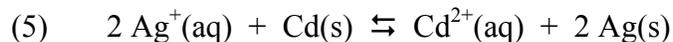


$$(4) \quad (E_{\text{cell}} = E^{\circ}_{\text{cell}} - (0.059 / n) \log ([C]^c [D]^d / [A]^a [B]^b))$$

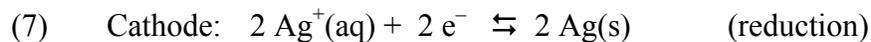
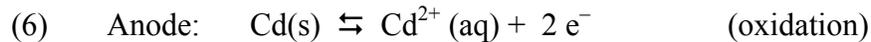
The Standard Potential Table in your textbook lists many half-cell reactions and their voltages. These potentials are measured relative to a selected standard half-reaction (usually the Standard Hydrogen Electrode (SHE): $2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2(\text{g})$, $E^{\circ} = 0.00 \text{ V}$). Typically, the reactions are listed as reductions. Therefore, the species most easily reduced have large *positive* voltage potentials and the species most easily oxidized have large *negative* potentials.

Cell notations (or cell diagrams) are a shorthand description of **galvanic** (spontaneous) **cells**. The reaction at the anode, cathode, reaction conditions (concentration, pressure etc.), and the type of electrode and electrode components are all described. By definition, oxidation takes place at the anode and reduction takes place at the cathode. Electrons flow from the anode to the cathode through the wire connecting the electrodes. (Typically, the anode is designated as the "negative" terminal (since electrons are produced at this terminal) and the cathode is called the "positive" terminal.)

Example: A galvanic cell is constructed from solutions in two beakers connected by a salt bridge and an external wire. One beaker contains 0.15 M $\text{Cd}(\text{NO}_3)_2$ and a Cd metal electrode. The other beaker contains 0.20 M AgNO_3 and Ag metal electrode. The net ionic equation for the cell reaction is:



In the reaction above, cadmium metal is oxidized (loses electrons) and is, therefore, the **anode**. The silver ion is reduced (gains electrons) to form Ag^0 (the **cathode**).



Using the rules listed below, cell notation is:



Cell Notation Rules:

1. The anode half-cell is described first; the cathode half-cell follows. Within a given half-cell, the reactants are specified first and products last. As the reader's eye proceeds from left to right the description of the oxidation reaction is first and the reduction reaction is last (in other words - the direction of electron flow). Spectator ions are not included.
2. A single vertical line (|) is drawn between two chemical species that are in different phases, but in physical contact with each other (*e.g.* solid electrode | liquid with electrolyte). A double vertical line (||) represents a salt bridge or porous membrane separating the individual half-cells.

The phase of each chemical (s, l, g, aq) is shown in parentheses. If the electrolytes in the cells are not at standard conditions, concentrations and/or pressure is included in parentheses with phase as shown in equation (8). If no concentration or pressure is noted, the electrolytes in the cells are assumed at standard conditions (1.00 M or 1.00 atm and 298 K).