Cell Potential

Cell Potential (E_{cell})

- **Cell potential (electromotive force, emf)** is the driving force in a galvanic cell that pulls electrons from the oxidation in one compartment to the reduction in the other.
- The **volt (V)** is the unit of electrical potential.
- Electrical charge is measured in **coulombs (C)**.
- A volt is 1 joule of work per coulomb of charge transferred: 1 V = 1 J/C.
- A **voltmeter** is a device which measures cell potential.

Standard Reduction Potentials

- The measured potential of a voltaic cell is affected by changed in concentration of the reactants as the reaction proceeds and by energy losses due to heating of the cell and external circuit.
- In order to compare the output of different cells, the standard cell potential ($E°_{cell}$) is obtained at 298 K, 1 atm for gases, 1 M for solutions, and the pure solid for electrodes.

- The Standard Hydrogen Electrode is considered the reference half-cell electrode, with a potential equal to **0.00 V**.
- It is obtained when platinum is immersed in 1 M $H^+(aq)$, through which $H_2(g)$ is bubbled.

The Standard Electrode (Half-Cell) Potential ($E_{half\text{-}cell}$)

- A standard electrode potential always refers to the half-reaction written as a ***reduction***.
- Oxidized form + $n\,e^- \rightarrow$ reduced form $E°_{half\text{-}cell}$
- If you need the oxidation, you will have to reverse the reaction
- Reversing a reaction **changes the sign** of the potential.
- $E°_{cell} = E°_{reduction} + E°_{oxidation}$

Thermodynamically favored reactions

- As the potential increases in value (more positive), the reaction is more likely to occur (Thermodynamically favored, spontaneouly occurs).
- $E°_{cell}$ must be positive for the cell to produce electricity.
- A substance will have a thermodynamically favored or *spontaneous* reaction with another substance of a lower $E°_{cell}$.
- Although some half-reactions must be manipulated with coefficients, NEVER MULTIPLY THE $E°_{cell}$ BY THE COEFFICIENT!!!

Galvanic Cell Problems

- Consider a galvanic cell based on the following reactions. For each give the balanced half cell reactions and calculate $E°_{cell}$.
- $Cu^{2+}_{(aq)} + Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$
- $Fe^{3+}_{(aq)} + Cu_{(s)} \rightarrow Fe^{2+}_{(aq)} + Cu^{2+}_{(aq)}$
- $Al\,(s) + Cd^{2+}(aq) \rightarrow Cd(s) + Al^{3+}(aq)$

Calculating an Unknown $E°_{half\text{-}cell}$ from $E°_{cell}$.

- A voltaic cell based on the reaction between aqueous Br_2 and vanadium (III) ions has
- $E°_{cell}$ = 1.39 V:
- $Br_2(aq) + 2V^{3+}(aq) + 2H_2O(l) \rightarrow 2VO^{2+}(aq) + 4H^+(aq) + 2Br^-(aq)$
- What is the standard electrode potential for the reduction of VO^{2+} to V^{3+}?

Line Notations.

- The components of the anode compartment are written to the left of the cathode compartment.
- Double vertical lines separate the half-cells and represents the wire and salt bridge.
- Within each half-cell, a single vertical line represents a phase boundary. A comma separates half-cell components in the same phase.
- Half-cell components appear in the same order as in the half-reaction, while electrodes appear at the extreme left and right of the notation.
- $Mg_{(s)}|Mg^{2+}_{(aq)}||Al^{3+}_{(aq)}|Al_{(s)}$
- $Fe_{(s)}|Fe^{2+}_{(aq)}||H^+, MnO_4^-{}_{(aq)}, Mn^{2+}_{(aq)}|Pt_{(s)}$

Describing a Galvanic Cell.

- A cell will always be thermodynamically favored, or spontaneous, in the direction that produces a positive cell potential.
- A complete description of a galvanic cell always includes four items:

- 1. The cell potential (always positive for a galvanic cell) and the balanced cell reaction.
- 2. The direction of electron flow, obtained by inspecting the half-reactions and using the direction that gives a positive $E°_{cell}$.

- 3. Designation of the anode and cathode.
- 4. The nature of each electrode and the ions present in each compartment. A chemically inert conductor is required if none of the substances participating in the half-reaction is a conducting solid.

Diagramming Voltaic Cells

- In one compartment of a voltaic cell is an acidic solution of $Cr(NO_3)_3$, and a chromium electrode; in the other, a tin bar dips into a $Sn(NO_3)_2$ solution. A KNO_3 salt bridge joins the half-cells.
- Diagram the cell, show balanced equations, and write the cell notation.

Description of a Galvanic Cell.

- Describe completely the galvanic cell based on the following half-reactions under standard conditions:

- $Ag^+ + e^- \rightarrow Ag$ $\quad E°_{cell} = 0.80\ V$ (1)
- $Fe^{3+} + e^- \rightarrow Fe^{2+}$ $\quad E°_{cell} = 0.77\ V$ (2)

- In addition, draw the cell and write the line notation.