

21 • Electrochemistry

BLUFFER'S GUIDE

- Electrochemistry is all oxidation-reduction chemistry.
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Oxidation: loss of e^- ; ox # increases
Reduction: gain of e^- ; ox # decreases
example: $Fe^{2+} + 2e^- \rightarrow Fe(s)$ (reduction)
- In a reaction, the **oxidizing agent** gets **reduced**; the **reducing agent** gets **oxidized**
- Balancing redox reactions:
oxidation number method
 - assign ox #'s to every atom
 - determine changes in ox #
 - balance changes
 - balance all atoms except H & O
 - balance O's (add H_2O 's)
 - balance H's (add H^+ 's)
 - adjust for basic solution if needed**half-reaction method.**
 - determine oxidation & reduction
 - write two separate half-reactions
 - balance all atoms except H & O
 - balance O's (add H_2O 's)
 - balance H's (add H^+ 's)
 - add e^- 's to more positive side
 - balance e^- 's between half-reactions
 - combine half-reactions
 - adjust for basic solution if needed
- Electricity can either **cause** a reaction (electrolysis, electrolytic cell) or can be **produced** by the reaction (Galvanic cell, electrochemical cell, Voltaic cell).
- Electrolysis / Electroplating**
coulomb (C) = an amount of charge
amp = current = charge per second
 $1 \text{ amp} \cdot 1 \text{ second} = 1 \text{ Coulomb}$
 $1 \text{ C} / \text{amp}\cdot\text{s}$
Faraday constant, F:
 $1 \text{ mole } e^- = 96,500 \text{ C}$
- Electrolysis calculations begin with amp·s
Example:
How many moles of copper metal can be plated using a 10 amp circuit for 30 s?
 $10 \text{ amp} \times 30 \text{ s} \times \frac{1 \text{ C}}{1 \text{ amp}\cdot\text{s}} \times \frac{1 \text{ mol } e^-}{96500 \text{ C}} \times \frac{1 \text{ mol Ag}}{1 \text{ mol } e^-} = 3.1 \times 10^{-3} \text{ mole Ag}$
- Spontaneous redox reactions (unlike electrolysis/electroplating) can simply occur (as in the ornament lab) or can be separated so the oxidation and reduction occur in different containers (half-cells). In this way, the electrons must move through an outside wire (this is an electrochemical cell—a battery).
- Every atom has a different “potential” to accept electrons... “reduction potential”
 $Ag^+(aq) + e^- \rightarrow Ag(s) \quad E^\circ = +0.80 \text{ v}$
 $Cd^{2+}(aq) + 2e^- \rightarrow Cd(s) \quad E^\circ = -0.40 \text{ v}$
These are measured by comparing every chemical to the same “standard half-cell.”
The reduction with the more positive E° value will occur as written; the other reaction will reverse (oxidation).
Ex: $2Ag^+ + Cd \rightleftharpoons 2Ag + Cd^{2+}$
The **difference** in the E° values is the voltage of a cell made using these two reactions.
Ex: $+0.80 \text{ v} - (-0.40 \text{ v}) = 1.20 \text{ volts}$
NOTE that you do not multiply the Cd voltage by 2. Comparing every cell to the same standard cell accounts for this.
- Any change that drives the reaction forward will **increase** the cell's voltage.
- In *all* electrochemical cells:
Oxidation occurs at the **Anode**
Reduction occurs at the **Cathode**