

# 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  $E^\circ$  value will occur as written; the other reaction will reverse (oxidation).  
*Ex:*  $2Ag^+ + Cd \rightleftharpoons 2Ag + Cd^{2+}$   
The **difference** in the  $E^\circ$  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**