

21 • Electrochemistry

BLUFFER'S GUIDE

1. 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)

2. In a reaction, the **oxidizing agent** gets **reduced**; the **reducing agent** gets **oxidized**.

3. 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

4. Electricity can either **cause** a reaction (electrolysis, electrolytic cell) or can be **produced by** the reaction (Galvanic cell, electrochemical cell, Voltaic cell).

5. **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:

$$1 \text{ mole } e^- = 96,500 \text{ C}$$

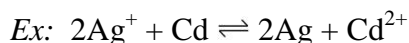
6. Electrolysis calculations begin with amp·s
Example:

$$\begin{aligned} &\text{How many moles of copper metal can be} \\ &\text{plated using a 10 amp circuit for 30 s?} \\ &10 \text{ amp} \times 30 \text{ s} \times \frac{1 \text{ C}}{1 \text{ amp}\cdot\text{s}} \times \frac{1 \text{ mol } e^-}{96500 \text{ C}} \times \frac{1 \text{ mol Ag}}{1 \text{ mol } e^-} = \\ &= 3.1 \times 10^{-3} \text{ mole Ag} \end{aligned}$$

7. Spontaneous redox reactions (unlike electrolysis/electroplating) can simply occur (as in rusting of Fe to Fe_2O_3) 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).

8. 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).



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.

9. Any change that drives the reaction forward will **increase** the cell's voltage.
10. In *all* electrochemical cells:
Oxidation occurs at the **Anode**
Reduction occurs at the **Cathode**

Acknowledgement: This page is adapted from a similar document from South Pasadena • AP Chemistry