Electrochemistry

Chemistry 30

Redox Reactions

- Redox = oxidation and reduction
- Originally, oxidation meant combination with oxygen (corrosion, combustion), but now means **loss of electrons**
- Reduction originally meant refining metal ores to pure metals, causing a reduction in mass, but now means **gain of electrons**
- In general, redox reactions occur when there is a transfer of electrons

Example: Redox

The single displacement reaction between copper and silver is:

$Cu\ (s) + 2\ AgNO_3\ (aq) \rightarrow 2\ Ag\ (s) + Cu(NO_3)_2\ (aq)$

a. Write the total and net ionic equations.
b. Which metal is being **oxidized**?
c. Which metal is being **reduced**?

Trick for Redox

LEO

the Lion Says

GER

LEO

Loss of Electrons is Oxidation

GER

Gain of Electrons is Reduction

Oxidation States/Numbers

- Positive/negative number for an atom or ion that reflects partial gain or loss of electrons
- Rules in reference book
- One oxidation number for EACH atom/ion, so must pay attention to subscripts, but coefficients (for balancing equation) do not matter

Example: Oxidation States

Determine the oxidation number for each element in the following compounds:

a. S_8
b. H^+
c. SnO_2
d. CO_3^{2-}
e. $Al_2(SO_4)_3$
f. $Na_3Co(NO_2)_6$

Identifying Redox Reactions

- Oxidation numbers can be used to identify if a reaction is a redox reaction
- If no elements change oxidation states between reactant and products, then no redox occurs

Example: Identifying Redox

Use oxidation numbers to determine if these are redox reactions.

a. $3\ Hg^{2+}\ (aq) + 2\ Fe\ (s) \rightarrow 3\ Hg_2\ (s) + 2\ Fe^{3+}\ (aq)$

b. $NaCl\ (aq) + AgNO_3\ (aq) \rightarrow AgCl\ (s) + NaNO_3$

Half-Reactions

- Breaks a full reaction apart into reduction equation and oxidation equation
- Example:

$$Zn\ (s) + 2\ HCl\ (aq) \rightarrow ZnCl_2\ (aq) + H_2\ (g)$$

becomes…

$$Zn\ (s) \rightarrow Zn^{2+}\ (aq) + 2\ e^-$$

$$2\ H^+\ (aq) + 2\ e^- \rightarrow H_2\ (g)$$

- Must be balanced by mass (atoms/ions) <u>and</u> charge

Example 1: Half-Reactions

$Zn\ (s) + Pb(NO_3)_2\ (aq) \rightarrow Pb\ (s) + Zn(NO_3)_2\ (aq)$

a. Write net ionic equation. (What is the spectator ion?)
b. Write the half-reaction for zinc.
c. Write the half-reaction for lead.
d. Identify which element is being oxidized and which is being reduced.

Example 2: Half-Reactions

Write both half-reactions, and identify which element is being oxidized and which is being reduced.

$$SnO_2\ (s) + C\ (s) \rightarrow Sn\ (s) + CO_2\ (g)$$

Acidic Conditions

- Means there is excess H^+ ions in the solution

To write:

- Create the half-reactions as usual
- Balance elements other than H and O
- Add H_2O to balance out oxygen atoms (to the opposite side of the arrow)
- Add H^+ to balance out hydrogen in the water molecules
- Add charges and put electrons on the proper side

Example: Acidic Conditions

Write the half-reaction for dichromate, $Cr_2O_7^{2-}$, forming chromium(III) ions in acidic solution.

Basic Conditions

- Means there is an excess of hydroxide ions
- As with other base calculations, more steps here

To write:

- Steps are the same as for acidic conditions, with one additional step:

  Add OH^- ions to both sides to balance all H^+
- Cannot end up with H^+ in your end reaction (bases have OH^-, not H^+)

Example 1: Basic Conditions

Change this half-reaction that is in acidic conditions to basic conditions:

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2\ H_2O$$

Example 2: Basic Conditions

Write the half-reaction for solid silver forming silver oxide in basic solution.

Balancing with Half-Reactions

- Break reaction into two half-reactions; remove spectator ions
- Balance each half-reaction separately, by mass and charge
- Compare both half-reactions so total number of e^- is equal for both (multiply each half-reaction by whole number)
- Add half-reactions together and add back spectator ions

Example 1: Balancing with HR

$Cu\ (s) + AgNO_3\ (aq) \rightarrow Cu(NO_3)_2\ (aq) + Ag\ (s)$

Example 2: Balancing with HR

$MnO_4^- + Fe^{2+} + H^+ \rightarrow Mn^{2+} + Fe^{3+} + H_2O$

Acidic Solutions

- Create half-reactions as usual, using steps for half-reactions in acidic conditions
- Balance electrons in both half-reactions, then add together
- Cancel common terms

Example: Acidic Solutions

Balance the following reaction in acidic conditions:

$Cr_2O_7^{2-}$ (aq) + HNO_2 (aq) → Cr^{3+} (aq) + NO_3^- (aq)

Basic Solutions

- Create half-reactions as usual, using steps for half-reactions in basic conditions
- Balance electrons in both half-reactions, then add together
- OH^- and H^+ ions (on the same side) combine to form water
- Cancel common terms

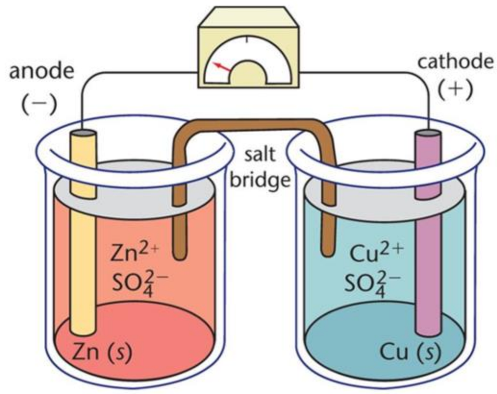
Example: Basic Solutions

Balance the following reaction in basic conditions:

$$Cu\ (s) + HNO_3\ (aq) \rightarrow Cu^{2+}\ (aq) + NO\ (g)$$

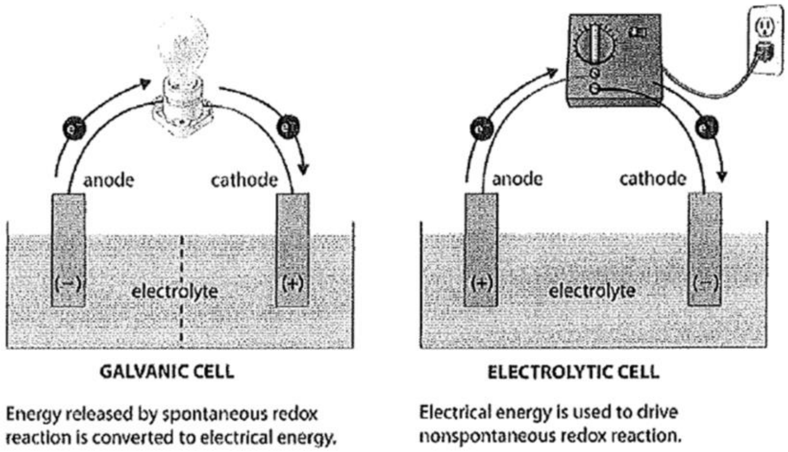
Galvanic Cells

- AKA voltaic cells
- Half-reactions are split into two separate cells, connected by a conducting material and a salt bridge.



https://www.youtube.com/watch?v=7b34XYgADlM

Electrochemical Cells



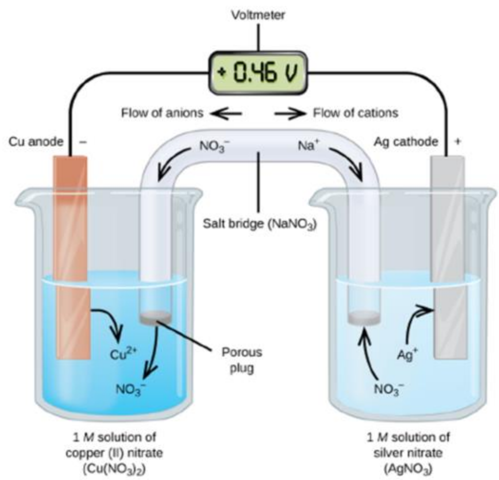
Galvanic (voltaic) cells	spontaneous oxidation-reduction reaction	Is separated into 2 half-cells	Electrodes made from metals (inert Pt or C if ion to ion or gas)	Battery – its cell potential drives the reaction and thus the e^-
Electrolytic cells	non-spontaneous oxidation-reduction reaction	Usually occurs in a single container	Usually inert electrodes	Battery charger – requires an external energy source to drive the reaction and e^-

Cell Notation

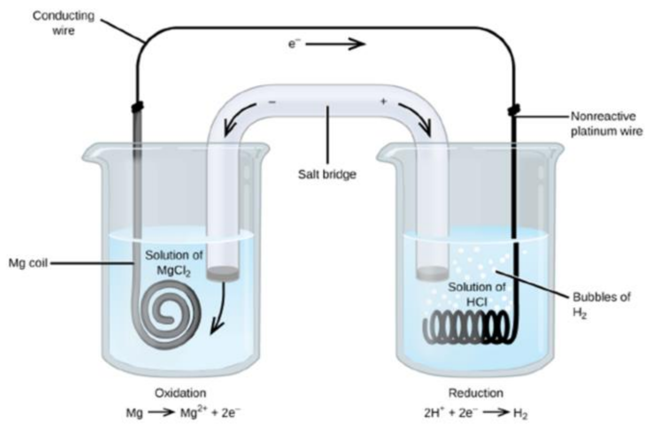
anode | electrolyte || electrolyte | cathode

- Anode is the site of oxidation (An Ox)
- Cathode is the site of reduction (Red Cat)
- When possible, include initial concentrations of electrolyte solutions
- | denotes a phase boundary
- || denotes the salt bridge

Example: Cell Notation



Example: Cell Notation



Example: Cell Notation

Consider the galvanic cell consisting of:

$$5\ Fe^{2+}\ (aq) + MnO_4^-\ (aq) + 8\ H^+\ (aq) \rightarrow$$
$$5\ Fe^{3+}\ (aq) + Mn^{2+}\ (aq) + 4\ H_2O\ (l)$$

Write the two half reactions, then write the reaction using cell notation.

$5\ Fe^{2+}$ (aq) → $5\ Fe^{3+}$ (aq) + 5 e^- (oxidation)
MnO_4^- (aq) + 8 H^+ (aq) + 5 e^-→ Mn^{2+} (aq) + 4 H_2O (l) (reduction)

Pt (s) | Fe^{2+} (aq), Fe^{3+} (aq) || MnO_4^- (aq), H^+ (aq), Mn^{2+} (aq) | Pt (s)

Standard Reduction Potential

- Indicates the tendency of an element to gain electrons
- In galvanic cells, identifies which element will be oxidized and which will be reduced
- Measured in volts, relative to reduction potential of hydrogen (0.0 V), at standard conditions (25°C, 1 atm, 1 mol/L solutions)
- ALL HALF-REACTIONS are written as reduction

Standard Reduction Potential

- The half-cell higher up the list (more positive) will be reduced; other will be oxidized

Cell Potential

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{reduction}} - E^{\circ}_{\text{oxidation}}$$

- For a galvanic cell, E_{cell} will be positive, meaning the reaction will occur spontaneously
  - Negative E_{cell} for electrolytic cells
- More positive reduction potential is reduced, lower is oxidized, for a galvanic cell

Example 1: Cell Potential

Determine the cell potential with a galvanic cell undergoing the following two half-reactions:

Zn^{2+} (aq) + 2 e^- → Zn (s)

Cu^{2+} (aq) + 2 e^- → Cu (s)

Example 2: Cell Potential

Determine the cell potential for the overall cell reaction. Is this cell spontaneous or non-spontaneous?

$2\ Al^{3+}\ (aq) + 3\ Cu\ (s) \rightarrow 3\ Cu^{2+}\ (aq) + 2\ Al\ (s)$

Example 3: Cell Potential

Determine the cell potential for the overall cell reaction. Is this cell spontaneous or non-spontaneous?

$$Cd\ (s) + 2\ NO_3^-\ (aq) + 4\ H^+\ (aq) \rightarrow Cd^{2+}\ (aq) + 2\ NO_2\ (g) + 2\ H_2O\ (l)$$

Example 4: Cell Potential

A galvanic cell is constructed with solid iron (making Fe^{3+} ions) and calcium.

a. Determine the anode and cathode, if the cell is spontaneous.
b. Write the cell notation.
c. Calculate the standard cell potential.

Galvanic Cell Description

Must include:

1. Cell potential and balanced cell reaction
2. Direction of electron flow
3. Designation of anode and cathode
4. Nature of each electrode and ions present in each compartment
    - A chemically inert conductor is required if none of the substances in the half-reaction is a conducting solid (e.g. Pt, C)

Example 1: Galvanic Cell

For the two half-reactions:

$$Zn\ (s) \rightarrow Zn^{2+}\ (aq) + 2\ e^-$$

$$Ag\ (s) \rightarrow Ag^{+}\ (aq) + e^-$$

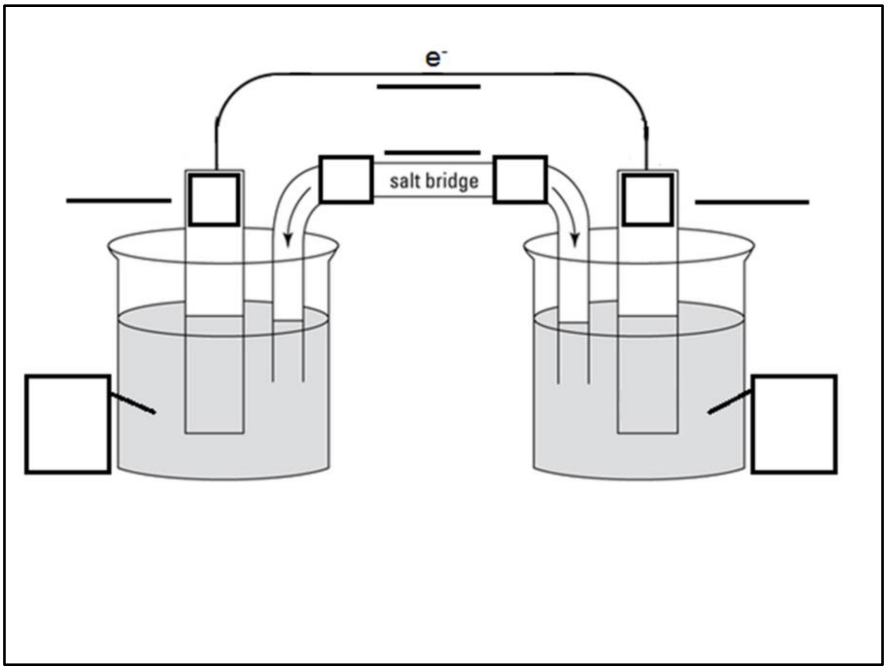
a. Write the half-reactions in cell notation.
b. Draw a diagram of the electrochemical cell, assuming is it spontaneous. Label the electrodes, electrolytes, direction of electron flow and direction of ion movement.
c. What would be a suitable substance for the salt bridge for this reaction?

Example 2: Galvanic Cell

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

$Ag^+ + e^- \rightarrow Ag$ $\quad E° = 0.80\ V$

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ $\quad E° = 0.77\ V$


e⁻
salt bridge