Electrochemistry

AP 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

Oxidation States/Numbers

- Positive/negative number for an atom or ion that reflects partial gain or loss of electrons
- 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. $3\ Hg^{2+}\ (aq) + 2\ Fe\ (s) \rightarrow 3\ Hg\ (s) + 2\ Fe^{3+}\ (aq)$

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 <u>both sides</u> 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

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

Example: Acidic Solutions

Balance the following reaction in acidic conditions:

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

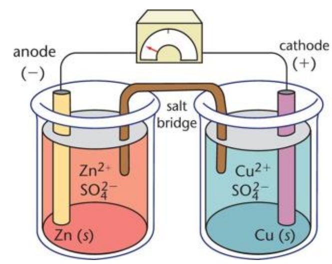
Example: Basic Solutions

Balance the following reaction in basic conditions:

Cu (s) + HNO_3 (aq) → 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.

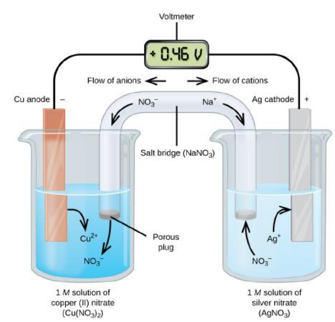


Cell Notation

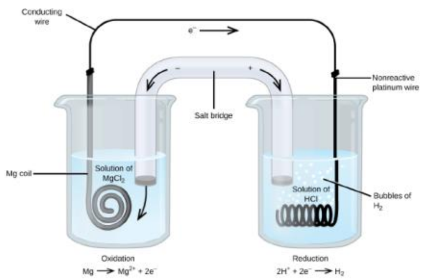
anode | electrolyte || electrolyte | cathode

- 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.

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

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
- More positive reduction potential is reduced, lower is oxidized

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

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

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

Galvanic Cell Description

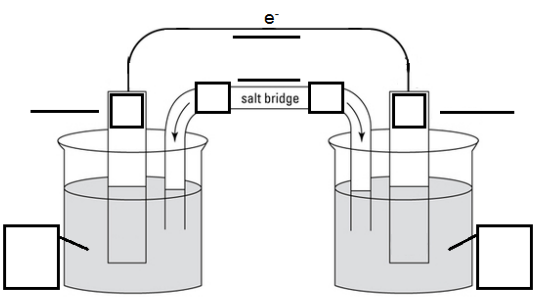
Must include:
1. Cell potential and balanced cell reaction
2. Direction of electron flow
3. Designation of anode and cathode
4. Nature of each electrode and ions present in each compartment
   - A chemically inert conductor is required if none of the substances in the half-reaction is a conducting solid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

Example: 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



Gibbs Free Energy

For standard conditions,

$$\Delta G° = -nFE°$$

Where:

n is mol of e^- transferred

F is the faraday, 96 485 C/mol e^-

E° is the standard cell potential in V (J/C)

Spontaneity of Cells

- If E_{cell} is positive, then ΔG is negative, which BOTH indicate a thermodynamically favourable (spontaneous) reaction

Example: Free Energy

Using a table of standard reduction potentials, use the value of ΔG to predict whether 1 M HNO_3 will dissolve gold metal to form a 1 M Au^{3+} solution.

Non-Standard Conditions

- Pressure, temperature or concentration changes from 1 atm, 25°C or 1 M…
- Concentration changes will shift whether forward/reverse reaction is favoured (Le Chatelier's Principle)
- [Product]/[Reactant]
  - > 1, reverse reaction is favoured
  - < 1, forward reaction is favoured

Example: Non-Standard Conditions

For the cell reaction:

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

Predict whether E_{cell} will be larger or smaller than $E°_{cell}$ for:

a. $[Al^{3+}] = 2.0$ M, $[Mn^{2+}] = 1.0$ M

b. $[Al^{3+}] = 1.0$ M, $[Mn^{2+}] = 3.0$ M

Example: Non-Standard Conditions

For the cell

$X\ (s) + Y^{2+}\ (aq) \rightarrow Y\ (s) + X^{2+}\ (aq)$

The concentration of the X ion is 0.20 M an the concentration of the Y ion is 0.30 M. Will E_{cell} increase, decrease or remain the same, relative to $E°_{cell}$?

Nernst Equation

- *Not on AP formula sheet, but useful*
- To quantitatively determine E_{cell} vs $E°_{cell}$

$$E = E° - \frac{RT}{nF} lnQ$$

R = 8.314 J/K·mol, F = 96 485 C/mol e^-

Q = $[products]^{coefficient}/[reactants]^{coefficient}$ (aqueous species only)

T = temperature in Kelvin

n = number of electrons exchanged

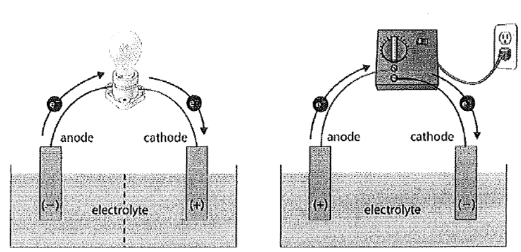
Example: Nernst Equation

For this reaction at 298 K:

$Co\ (s) + Fe^{2+}(aq,\ 1.94\ M) \rightarrow Co^{2+}\ (aq,\ 0.15\ M) + Fe\ (s)$

Calculate E_{cell} to determine if the reaction is spontaneous.

Electrochemical Cells



GALVANIC CELL

Energy released by spontaneous redox reaction is converted to electrical energy.

ELECTROLYTIC CELL

Electrical energy is used to drive nonspontaneous redox reaction.

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^-

Electrolysis

- Non-spontaneous – requires electricity from external source
- Questions to know how to solve:
  - How long will it take?
  - How much can be produced?
  - What current must be used?
- 1 A = 1 C/s
- 1 F = 96 500 C/mol e^-

Example: Electrolysis

If liquid titanium(IV) chloride (acidified with HCl) is electrolyzed by a current of 1.000 A for 2.000 h, how many grams of titanium will be produced?