

Electrochemistry -- Chapter 19

1. Oxidation & Reduction (Redox) Reactions

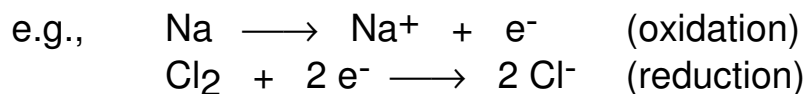
Redox reaction -- electron transfer process



Overall process involves *two Half Reactions*:

oxidation -- loss of electron(s)

reduction -- gain of electron(s)



related terms:

oxidizing agent = the substance that is reduced (Cl_2)

reducing agent = the substance that is oxidized (Na)

Oxidation and reduction always occur together so that there is no *net* loss or gain of electrons overall.

2. Oxidation Numbers (oxidation states)

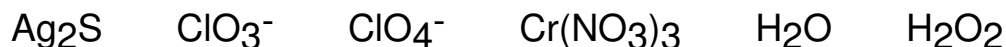
Oxidation Number -- a "charge" that is *assigned* to an atom to aid in balancing redox reactions

Generally, oxidation number is the charge that would result if all of the bonding electrons around an atom were assigned to the more electronegative element(s).

Rules for assigning oxidation numbers -- see page 177

Learn the rules by working examples !

e.g., assign all oxidation numbers in:



3. **ION-ELECTRON METHOD** for Balancing Redox Equations

1. Write unbalanced *ionic* equations for the two half-reactions. (Look at oxidation numbers in the "skeleton equation")
2. Balance atoms other than H and O.
3. Balance O with H₂O.
4. Balance H with H⁺.
5. Balance charge with appropriate number of electrons.
6. If in acidic solution, then skip to step 7. If in basic solution, then add equal number of OH⁻ to both sides to cancel all of the H⁺.
7. Rewrite the balanced half reactions.
8. Multiply balanced half-reactions by appropriate coefficients so that the number of electrons are equal.
9. Add the half-reactions together.
10. Cancel species that appear on both sides to get the balanced Net Ionic Equation.
11. If necessary, add spectator ions to get the balanced molecular equation.

Check the Final Balance (atoms and charges) !

Work Many Examples !!!

4. **Electrochemical Cell** a device that converts electrical energy into chemical energy or vice versa

Two Types

electrolytic cell

converts electrical energy into chemical energy
electricity is used to drive a *non-spontaneous reaction*

galvanic (or voltaic) cell

converts chemical energy into electricity (a battery!)
a *spontaneous reaction* produces electricity

Conduction

metals *metallic* (electronic) conduction
free movement of electrons

solutions
(or molten salts) *electrolytic* (ionic) conduction
free movement of ions

5. **Electrolysis** -- chemical reactions that occur during electrolytic conduction

e.g., molten NaCl -- [see Figure 19.23](#)

reduction $\text{Na}^+ + \text{e}^- \longrightarrow \text{Na}$
Na⁺ ions migrate toward the negative electrode
and are reduced

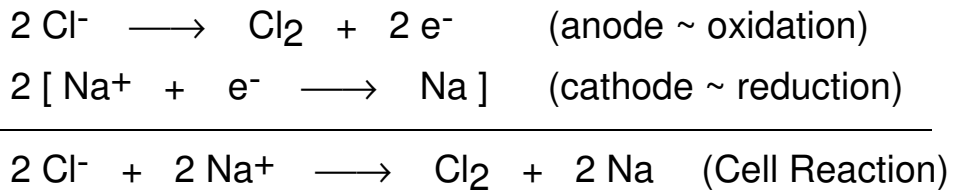
oxidation $2 \text{Cl}^- \longrightarrow \text{Cl}_2 + 2 \text{e}^-$
Cl⁻ ions migrate toward the positive electrode
and are oxidized

electrodes

cathode -- where **reduction** occurs

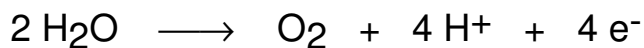
anode -- where **oxidation** occurs

Net Cell Reaction -- add anode & cathode half-reactions
so that # electrons cancel

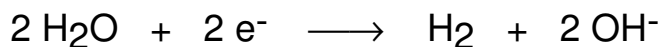


but, *in aqueous solution*, electrolysis of water may occur:

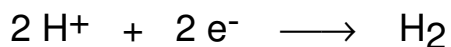
oxidation ($\text{H}_2\text{O} \rightarrow \text{O}_2$)



reduction ($\text{H}_2\text{O} \rightarrow \text{H}_2$) -- in *neutral or basic solution*



reduction ($\text{H}^+ \rightarrow \text{H}_2$) -- in *acidic solution*



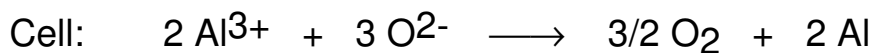
6. Some Industrial Applications of Electrolysis

Preparation of Aluminum from molten Al_2O_3

(can't use Al^{3+} in solution since H_2O is easier to reduce)

anode: $3 [\text{O}^{2-} \longrightarrow 1/2 \text{O}_2 + 2 \text{e}^-]$

cathode: $2 [\text{Al}^{3+} + 3 \text{e}^- \longrightarrow \text{Al}]$



Electroplating reduction of metal ions (from solution)
to pure metals (Ag, Cr, Cu, etc.)

e.g.,



7. Quantitative aspects of Electrolysis ~ the Faraday

e.g., consider a cell with the above cathode reaction

Stoichiometry: 1 mole Cr^{3+} ~ 3 moles e^{-} ~ 1 mole Cr

if a current equivalent to 3 moles of electrons is passed
through the solution of Cr^{3+} , then 1 mole of Cr metal
will be produced

by definition: 1 Faraday (F) = 1 mole electrons

but, how much electrical current is this?

$$1 \text{ F} = 96,500 \text{ coulombs}$$

and,

$$1 \text{ coulomb} = 1 \text{ amp sec}$$

Problem :

How long would it take to produce 25 g of Cr from
a solution of Cr^{3+} by a current of 2.75 amp?

1 mole Cr ~ 3 moles e^{-} ~ 3 F ~ 3 x 96,500 coulombs

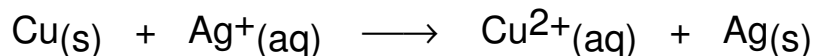
$$25 \text{ g Cr} \times \frac{1 \text{ mole Cr}}{52 \text{ g Cr}} \times \frac{3 \text{ F}}{1 \text{ mole Cr}} = 1.44 \text{ F}$$

$$1.44 \text{ F} \times \frac{96,500 \text{ coulombs}}{\text{F}} = 139,000 \text{ coulombs}$$

$$\frac{139,000 \text{ amp sec}}{2.75 \text{ amp}} \times \frac{1 \text{ hr}}{3600 \text{ sec}} = \underline{14.0 \text{ hr}}$$

8. **Galvanic Cells** (batteries) -- produce electrical energy

e.g., a spontaneous reaction:



[Ag metal will be deposited on a Cu wire dipped into aqueous AgNO₃ solution.]

in a galvanic cell, the half reactions are occurring in separate compartments (half-cells) -- see [Figure 19.22](#)

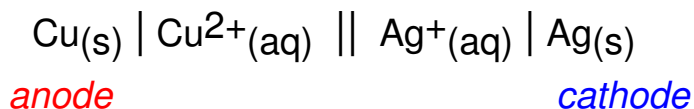
Charges on the electrodes

Galvanic cell (+) cathode ~ reduction
 (-) anode ~ oxidation

Electrolytic cell (+) anode ~ oxidation
 (-) cathode ~ reduction

Cell Notation -- summary of cell description

e.g.,



9. **Cell Potential** ~ E°_{cell} (an *electromotive force*, emf)

units of E°_{cell} are volts (1 volt = 1 joule / coulomb)

E°_{cell} is a measure of the relative spontaneity of a cell reaction

positive (+) E°_{cell} \longrightarrow spontaneous reaction

E°_{cell} depends on

- nature of reactants
- temperature -- superscript $^\circ$ means 25°C
- concentrations -- superscript $^\circ$ means all are 1.00 M and all gases are 1.00 atm

but, E°_{cell} is *independent* of amounts of reactants

10. Standard Potentials

Standard Reduction Potential

the potential of a half-cell relative to a standard reference

Some examples	E° (volts)
$\text{F}_2(\text{g}) + 2 \text{e}^- \longrightarrow 2 \text{F}^-(\text{aq})$	+ 2.87
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Fe}^{2+}(\text{aq})$	+ 0.77
$2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2(\text{g})$	0.00 (ref)
$\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Fe}(\text{s})$	- 0.44
$\text{Li}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Li}(\text{s})$	- 3.05

Ease of Reduction ~ increases with E°

e.g., F_2 is easiest to reduce, Li^+ is the hardest

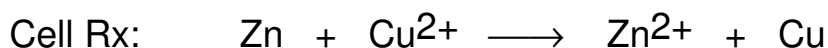
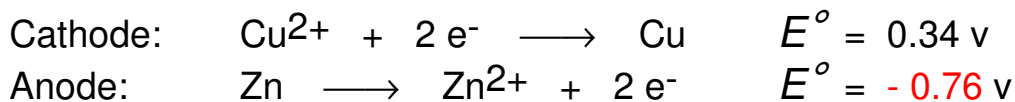
Standard Cell Potential ~ E°_{cell} can be determined from standard reduction potentials:

$$E^\circ_{\text{cell}} = E^\circ_{\text{oxid}} + E^\circ_{\text{red}}$$

Change the sign for E°_{oxid} relative to value in the table of reduction potentials!

Some Problems involving Standard Potentials

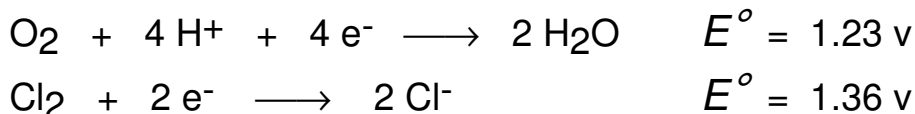
- (1) Is the following a galvanic or an electrolytic cell?
Write the balanced cell reaction and calculate E°_{cell} .



$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{oxid}} + E^\circ_{\text{red}} = (+0.76 \text{ v}) + 0.34 \text{ v} \\ &= +1.10 \text{ v} \quad \therefore \text{Galvanic} \end{aligned}$$

Note the sign change for the E°_{oxid} value!

- (2) Given the standard reduction potentials:



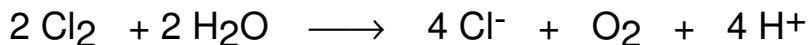
Write a balanced equation and calculate E°_{cell} for a *galvanic cell* based on these half reactions.

“galvanic” implies a *positive* value for E°_{cell}

so, $\text{Cl}_2 / \text{Cl}^-$ should be the reduction half reaction,

since $1.36 - 1.23 = +0.13 \text{ v}$

\therefore reverse the O_2 half reaction and make it the oxidation
multiply the Cl_2 reaction by 2, to make e⁻'s cancel, hence:



Note: When a half-reaction is multiplied by a coefficient, the E° VALUE IS NOT MULTIPLIED by the coefficient.

11. Cell Potential and Thermodynamics

Free Energy Change (ΔG)

$$\Delta G = -W_{\max} \quad (\text{maximum work})$$

for an electrochemical cell:

$$W = n F E_{\text{cell}} \quad \begin{array}{l} n = \# \text{ moles } e^- \\ F = 96,500 \text{ coul/mole } e^- \end{array}$$

$$\text{units: } \quad \text{volt} = \text{joule/coul}$$

$$\text{joules} = (\text{moles } e^-) (\text{coul/mole } e^-) (\text{joule/coul})$$

\therefore free energy is related to E_{cell} as follows

$$\Delta G = -n F E_{\text{cell}}$$

under standard conditions: use ΔG° and E°_{cell}

12. Equilibrium Constant

$$\text{since, } \Delta G^\circ = -RT \ln K_c = -n F E^\circ_{\text{cell}}$$

can rearrange to:

$$E^\circ_{\text{cell}} = \frac{RT}{nF} \ln K_c$$

at 25°C, use values for R, T, and F, convert to base-10 log:

$$E^\circ_{\text{cell}} = \frac{0.0592}{n} \log K_c$$

13. Effect of Concentration on Cell Potential

for a general reaction:



$$\Delta G = \Delta G^\circ + RT \ln Q$$

where, Q = "concentration quotient"

$$= \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \{\text{use given concentrations}\}$$

since, $\Delta G = -n F E$:

$$-n F E = -n F E^\circ + RT \ln Q$$

rearrange, to get the "Nernst Equation"

$$E = E^\circ - [RT / nF] \ln Q$$

The Nernst Equation shows the relationship between the standard cell potential (E°) and the cell potential (E) under actual, non-standard conditions.

this can be simplified at 25°C to:

$$E = E^\circ - (0.0592 / n) \log Q$$

major use of the Nernst Equation:

- determine E°_{cell} from standard reduction potentials
- use actual concentrations (i.e., Q) to calculate E_{cell}