Chapter 20: Electrochemistry I

Chem 102
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Electrochemistry

- The study of the relationships between electrical processes and chemical processes.
- Applications: batteries, electroplating, fuel cells, hydrogen production, biological processes.




Electrochemistry

Electrical energy

Interconversion

Chemical energy

Electrochemical processes:

- Oxidation-reduction (redox) processes, which involve electron transfers from one substance to another
- Energy released by a spontaneous chemical reaction is converted into electricity (e.g., battery)
- Electrical energy can be used to force a non-spontaneous reaction to occur (e.g., electrolysis)

Basics of electricity

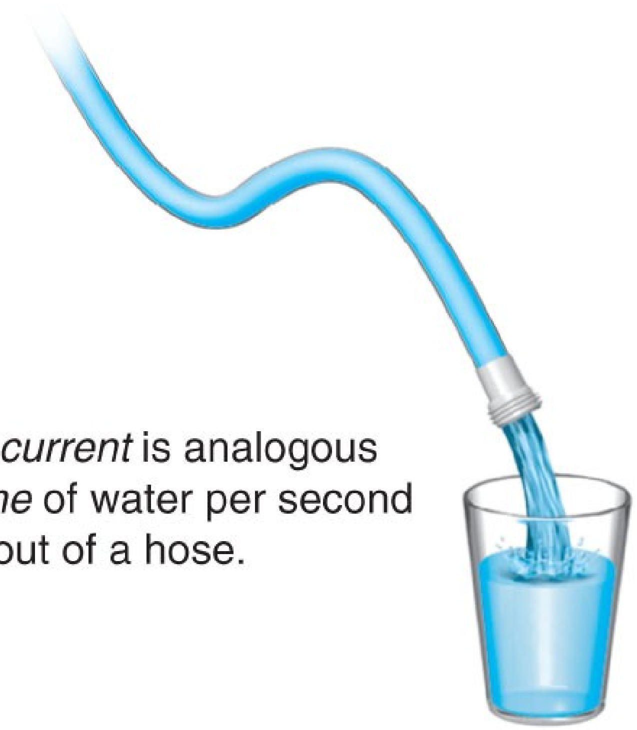
<u>Voltage</u> (*U*) is the potential energy per electron (Volts; V)

<u>Work</u> is the electron potential energy times the total charge moved (Joules; J): $w = U \times q_{tot}$

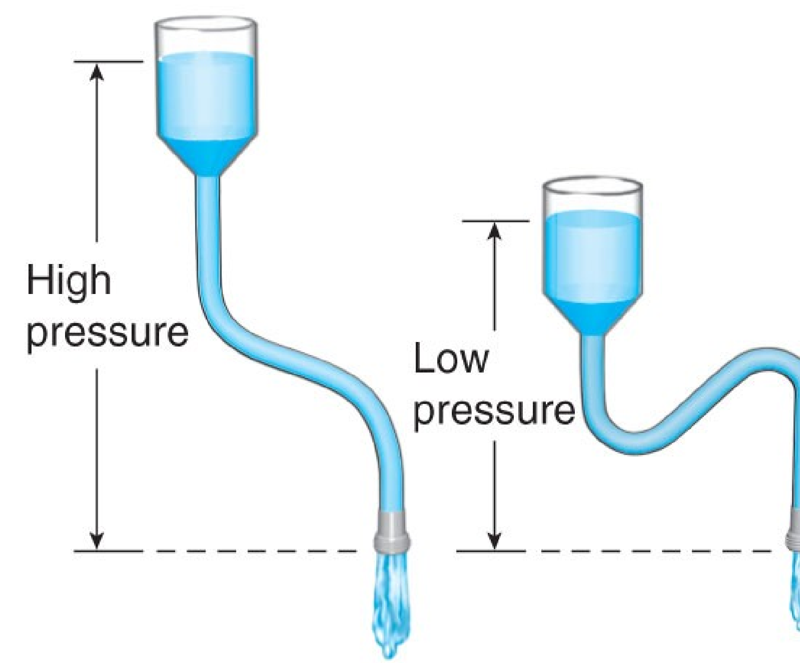
<u>Current</u> (*I*) represents the number of electrons passing through per second (Amperes; A)

<u>Resistance</u> (Ohm's law) is $R = U / I$ (Ohm or Ω; "load")

<u>Power</u> is $P = U \times I$ (Watts)



Electric *current* is analogous to *volume* of water per second flowing out of a hose.



Electric *potential difference* is analogous to the hydrostatic *pressure* pushing water through a hose. High pressure gives high flow.

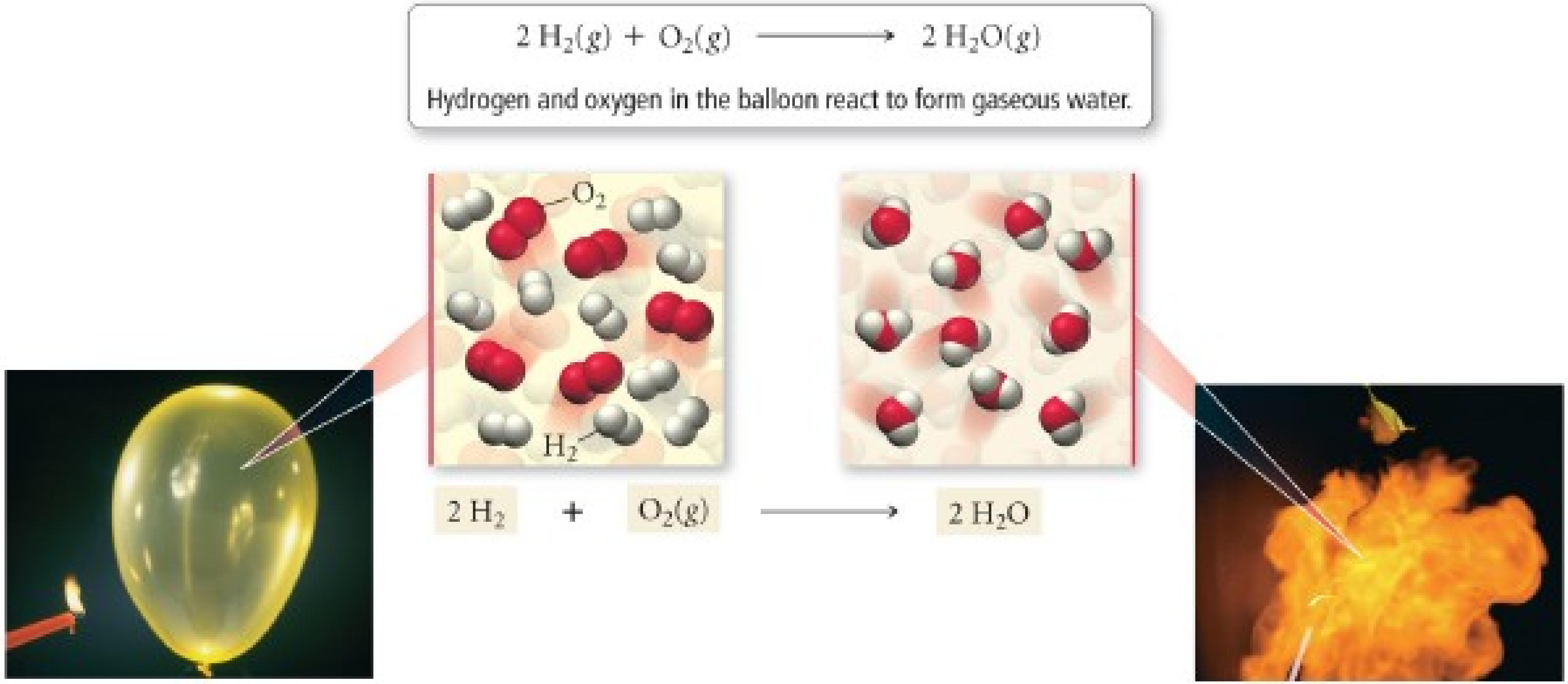
Oxidation-reduction reactions (redox reactions)

Redox reactions involve the *transfer of electrons* from one atom/molecule to another.

Example: $4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$

Electrons are transferred from iron to oxygen.

Combustion as a redox reaction



Redox reactions

- Reacting atoms gain or lose electrons:

  If one loses one (or more) electron, another must gain one (or more) electron.
- Atoms that **lose** electrons are being **oxidized**.
- Atoms that **gain** electrons are being **reduced**.
- **LEO GER:**

  Loss of electrons is oxidation, gain of electrons is reduction
- **OIL RIG:**

  Oxidation is loss of electrons, reduction is gain of electrons

Redox reactions

Or: oil rig

Example:

$$2\mathrm{Na} + \mathrm{Cl_2} \rightarrow 2\mathrm{NaCl}$$

$$2\mathrm{Na} \rightarrow 2\mathrm{Na}^+ + 2e^- \qquad \text{Ox}$$

$$\mathrm{Cl_2} + 2e^- \rightarrow 2\mathrm{Cl}^- \qquad \text{Red}$$

Oxidation: loosing electrons
Reduction: gaining electrons

Keeping track of electron transfer

- *Oxidation state*:
  - Oxidation states are <u>not</u> polyatomic ion charges
  - Oxidation states are <u>imaginary</u> charges based on a set of rules (next slide)
  - However, ion charges are <u>real and measurable</u>

- Oxidation states are written -1, -2, +2, etc. or roman letters
- Ion charges are written as superscripts 1-, 2-, 2+, etc.

Oxidation state rules

rules for assigning oxidation states (in order of priority)

1. free elements have an oxidation state = 0
   - $Na = 0$, $Cl_2 = 0$
2. monatomic ions have an oxidation state = charge
   - NaCl: $Na = +1$, $Cl = -1$
3. the sum of the oxidation states of all atoms in a...
   - (a) ...compound = 0
   - (b) ...polyatomic ion = charge on the ion
4. metals:
   - (a) Group 1 metals have an oxidation state = +1
   - (b) Group 2 metals have an oxidation state = +2
5. non-metals have oxidation states following table on next slide

Oxidation state rules

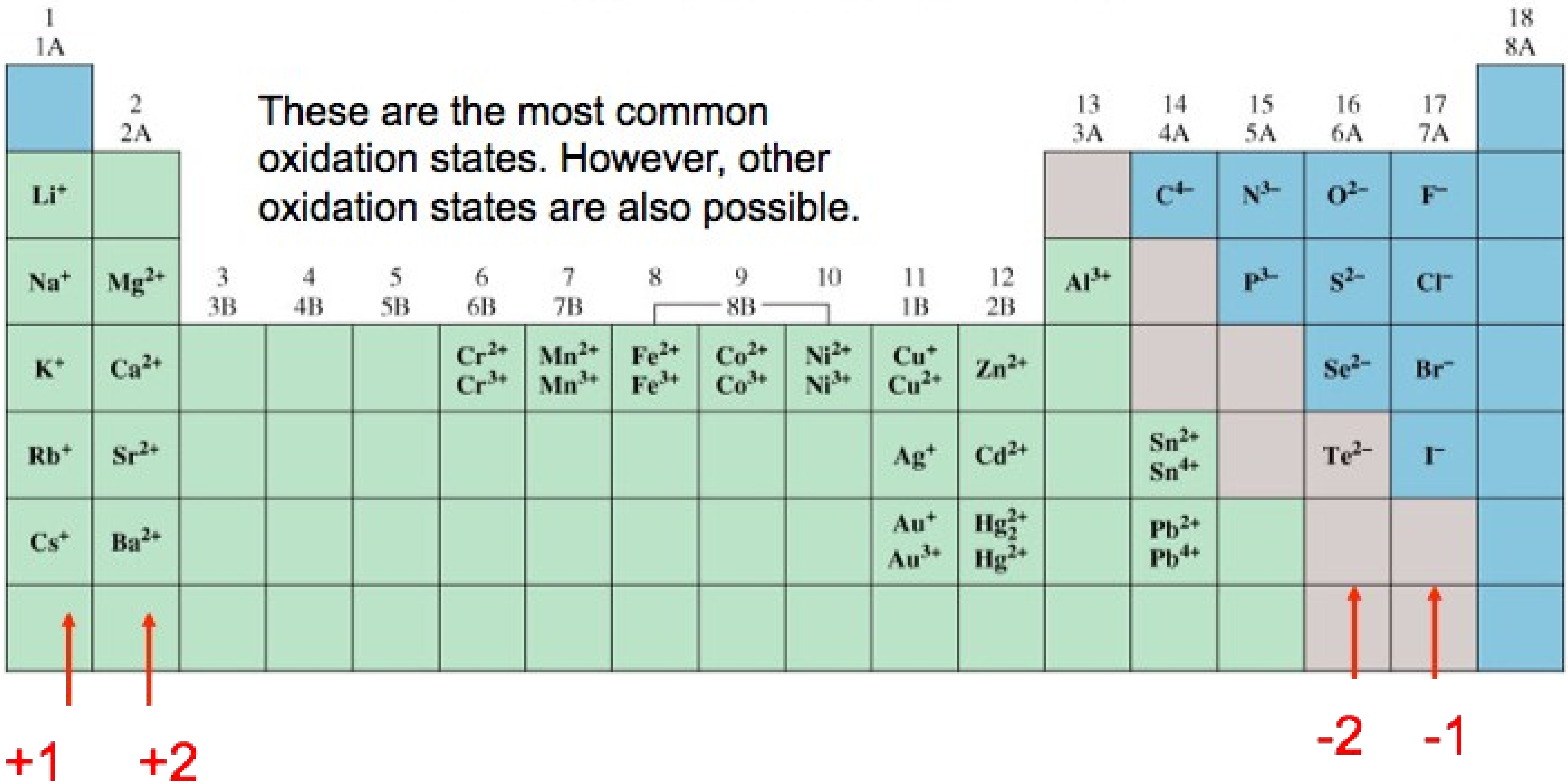
5. non-metals have oxidation states following this table
   - higher on table takes higher priority

nonmetal	oxidation state	example
F	-1	CF_4
H	+1	CH_4
O	-2	CO_2
Group 7A	-1	CCl_4
Group 6A	-2	CS_2
Group 5A	-3	NH_3

Practice: Assign oxidation states

- Br_2 (Hint: element; 0)
- K^+ (Hint: monoatomic ion; +1)
- LiF (Hint: both are monoatomic ions; +1 & -1)
- CO_2 (Hint: O atom is -2 then C is +4)
- SO_4^{2-} (Hint: O atom is -2 and total is -2 then S is +6)

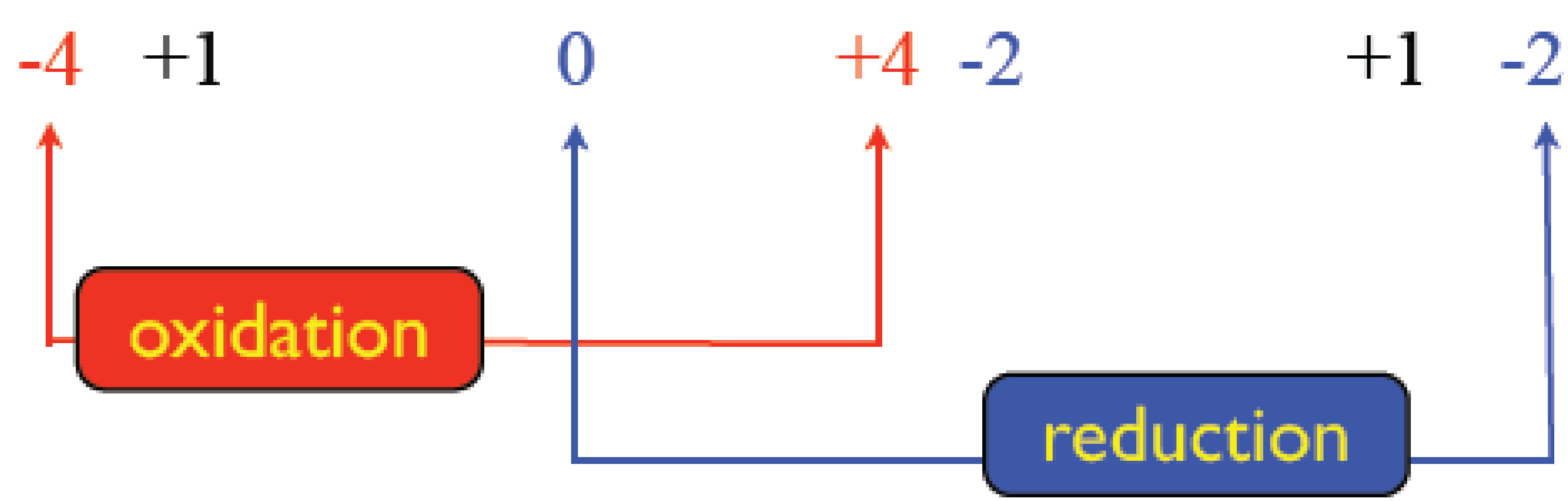
Common oxidation states



Oxidation and reduction - another definition

- **Oxidation**: an atom's oxidation state **increases**
- **Reduction**: an atom's oxidation state **decreases**

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$$



Oxidizing and reducing agents

- Oxidation and reduction must occur simultaneously
- The reactant that reduces an atom is called the reducing agent

  The reducing agent contains the element that is oxidized
- The reactant that oxidizes an atom is called the oxidizing agent

  The oxidizing agent contains the element that it reduced

$$2\mathrm{Na}(s) + \mathrm{Cl}_2(g) \rightarrow \mathrm{NaCl}(s)$$

$$\text{Na is oxidized, Cl is reduced}$$

$$\text{Na is the reducing agent, Cl}_2 \text{ is the oxidizing agent}$$

Oxidation and reduction half-reactions

$$\overset{0}{2Mg}\ (s) + \overset{0}{O_2}\ (g) \longrightarrow 2\overset{2+}{Mg}\overset{2-}{O}\ (s)$$

This reaction can be split into two *half-reactions*

Oxidation half-reaction
reactant (= reducing agent) *loses* e^-

$$2\ Mg \rightarrow 2\ Mg^{2+} + 4\ e^-$$

Reduction half-reaction
Reactant (= oxidizing agent) *gains* e^-

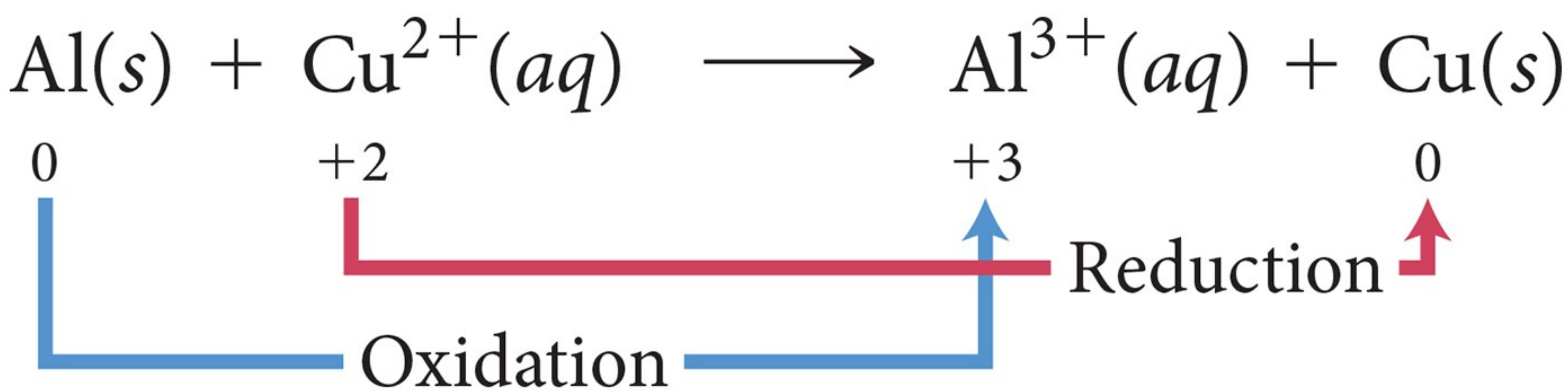
$$O_2 + 4\ e^- \rightarrow 2\ O^{2-}$$

Balancing Redox Equations

The “Half-reaction method” from Tro (7 steps):

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

1. Assign oxidation states to all atoms and identify the substances being oxidized and reduced:



Balancing Redox Equations

2. Separate the overall reaction into two half-reactions: one for oxidation, one for reduction:

$$\text{Oxidation: } Al(s) \rightarrow Al^{3+}(aq)$$
$$\text{Reduction: } Cu^{2+}(aq) \rightarrow Cu(s)$$

3. Balance each half-reaction with respect to **mass** in the following order:
   A. Balance all elements other than H and O
   B. Balance O by adding H_2O
   C. Balance H by adding H^+

Balancing Redox Equations

4. Balance each half-reaction with respect to **charge** by adding electrons:

$$Al(s) \rightarrow Al^{3+}(aq) + 3e^-$$

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

Balancing Redox Equations

5. Make the number of electrons in both half-reactions equal by multiplying one or both half-reactions by a small whole number:

$$2[Al(s) \rightarrow Al^{3+}(aq) + 3e^-]$$

$$2Al(s) \rightarrow 2Al^{3+}(aq) + 6e^-$$

$$3[Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)]$$

$$3Cu^{2+}(aq) + 6e^- \rightarrow 3Cu(s)$$

Balancing Redox Equations

6. Add the two half-reactions together, canceling electrons and other species as necessary:

$$2Al(s) \rightarrow 2Al^{3+}(aq) + \cancel{6}\cancel{e^-}$$

$$3Cu^{2+}(aq) + \cancel{6}\cancel{e^-} \rightarrow 3Cu(s)$$

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

Balancing Redox Equations

7. Verify that the reaction is balanced both with respect to mass and with respect to charge:

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

Reactants	Products
2 Al	2 Al
3 Cu	3 Cu
+6 Charge	+6 Charge

Balancing redox reactions in acidic solution

$$Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) \rightarrow Fe^{3+}(aq) + Cr^{3+}(aq)$$

1. Assign oxidation states to all atoms and identify the substances being oxidized and reduced.

Oxidation numbers: Fe^{2+} is +2, Fe^{3+} is +3, Cr^{3+} is +3.

For $Cr_2O_7^{2-}$: O is -2 and the sum must be -2, so:

$7 \cdot (-2) + 2x = -2$, which gives $x = 6$. Thus Cr is +6.

Cr is reduced (+6 to +3) and Fe (+2 to +3) is oxidized.

Balancing redox reactions in acidic solution

$$Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) \rightarrow Fe^{3+}(aq) + Cr^{3+}(aq)$$

2. Separate the overall reaction into two half-reactions: one for oxidation, one for reduction.

<u>Oxidation:</u> $Fe^{2+} \rightarrow Fe^{3+}$ (no further balancing in #3)

<u>Reduction:</u> $Cr_2O_7^{2-} \rightarrow Cr^{3+}$ (*not mass balanced*)

Balancing redox reactions in acidic solution

$$Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) \rightarrow Fe^{3+}(aq) + Cr^{3+}(aq)$$

3. Balance each half-reaction with respect to **mass** in the following order:
   A. Balance all elements other than H and O:
   $Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$
   B. Balance O by adding H_2O:
   $Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$
   C. Balance H by adding H^+:
   $Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$

Balancing redox reactions in acidic solution

$$Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) \rightarrow Fe^{3+}(aq) + Cr^{3+}(aq)$$

4. Balance each half-reaction with respect to **charge** by adding electrons:

<u>Oxidation:</u> $Fe^{2+} \rightarrow Fe^{3+} + e^-$

<u>Reduction:</u> Start with $Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$. So, +12 on the left and +6 on the right and balance as: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$. Note that the consumption of H^+ requires acidic solution!

Balancing redox reactions in acidic solution

$$Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) \rightarrow Fe^{3+}(aq) + Cr^{3+}(aq)$$

5. Make the number of electrons in both half-reactions equal by multiplying one or both half-reactions by a small whole number (here the first eq multiplied by 6):

$6Fe^{2+} \rightarrow 6Fe^{3+} + 6e^-$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

Balancing redox reactions in acidic solution

$$Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) \rightarrow Fe^{3+}(aq) + Cr^{3+}(aq)$$

6. Add the two half-reactions together, canceling electrons and other species as necessary:

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

Balancing redox reactions in acidic solution

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

7. Verify that the reaction is balanced both with respect to mass and with respect to charge.

Reactants	Products
6 Fe	6 Fe
2 Cr	2 Cr
7 O	7 O
14 H	14 H
Charge +24	Charge +24

Balancing redox reactions in basic solution

3. Balance each half-reaction with respect to **mass** in the following order:
   A. Balance all elements other than H and O
   B. Balance O by adding H_2O
   C. Balance H by adding H^+
   D. Neutralize H^+ by adding enough OH^- to neutralize each H^+. Add the same number of OH^- ions to each side of the equation. $H^+ + OH^- \rightarrow H_2O(l)$

Practice example

Balance the following reaction in basic solution:

$$MnO_4^-(aq) + Br^-(aq) \rightarrow MnO_2(s) + BrO_3^-(aq)$$

$$H_2O(l) + 2MnO_4^-(aq) + Br^-(aq) \rightarrow 2MnO_2(s) + BrO_3^-(aq) + 2OH^-(aq)$$