# REDOX INTRODUCTION

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## Oxidation-Reduction Reactions

Also known as ‘redox’ reactions.

These reactions always occur as a pair where electrons are transferred from one atom to another.

LEO the lion says GER

OILRIG

# REDOX INTRODUCTION

## Example #1

Identify the atoms being oxidized or reduced.

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

Reduction

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

Oxidation

c) $2\ Na + Cl_2 \rightarrow 2\ NaCl$

Oxidation of Na

Reduction of $Cl_2$

# Redox Reactions

These reactions may also be interpreted as one reactant causing a change in the other reactant.

oxidizing agent – the reactant which caused the other to be oxidized (this reactant is reduced)

reducing agent – the reactant which caused the other to be reduced (this reactant is oxidized)

# REDOX INTRODUCTION

## Example #2

For the following reactions:

i. Which element is oxidized? reduced?

ii. Identify the oxidizing agent. Reducing agent.

a) $2\ Ca + O_2 \rightarrow 2\ CaO$

Oxidized Reduced

Ca: Reducing agent

$O_2$: Oxidizing agent

b) $Mg + Br_2 \rightarrow MgBr_2$

Oxidized Reduced

Mg: Reducing agent

$Br_2$: Oxidizing agent

# OXIDATION NUMBERS

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Oxidation numbers are used to keep track of electrons during reactions.

It is an arbitrary system based on:

a) ions charge of an atom

b) electronegativity

For any <u>neutral compound</u>, the oxidation numbers of the atoms must <u>add up to zero.</u>

# OXIDATION NUMBERS

## Oxidation Numbers

| Atom or Ion | Oxidation Number | Examples |
|---|---|---|
| compounds containing a single type of atom | 0 | Na<br>$Cl_2$ |
| H in most compounds | +1 | HCl |
| H in a hydride | -1 | LiH |
| O in most compounds | -2 | $H_2O$ |
| O in a peroxide | -1 | $H_2O_2$ |
| monatomic ions | charge of ion | $Na^+ = +1$<br>$S^{2-} = -2$ |

# Oxidation Numbers

General steps to assign oxidation numbers:

1) Assign common oxidation numbers.
   – use your periodic table!!

2) The total oxidation number of a molecule or an ion is the value of the charge of the molecule or ion.

3) Unknown oxidation numbers can be assigned algebraically.

# OXIDATION NUMBERS

## Example #3

Determine the oxidation numbers for:

a) $H_2S$

+1 -2

b) $H_2O$

+1 -2

c) $ClO_2^-$

+3 -2

# OXIDATION NUMBERS

## Example #3

d) $SO_3^{2-}$

$+4 \quad -2$

e) $Na_3N$

$+1 \quad -3$

f) $H_2O_2$

$+1 \quad -1$

# OXIDATION NUMBERS

In a redox reaction, the oxidation numbers of atoms are expected to change.

Oxidation is an [illegible] in oxidation number.

Reduction is a [illegible] in oxidation number.

# OXIDATION NUMBERS

## Example #4

For the following reaction:

i. identify the substance oxidized / reduced

ii. oxidizing / reducing agents

$$\overset{+1\,-1}{2\,KCl} + \overset{+4\,-2}{MnO_2} + \overset{+1\,+6\,-2}{2\,H_2SO_4} \rightarrow \overset{+1\,+6\,-2}{K_2SO_4} + \overset{+2\,+6\,-2}{MnSO_4} + \overset{0}{Cl_2} + \overset{+1\,-2}{H_2O}$$

oxidation

reduction

**i. Cl atoms in KCl are oxidized (-1 to 0). Mn atoms in $MnO_2$ are reduced (+4 to +2)**

**ii. KCl is a reducing agent. $MnO_2$ is the oxidizing agent.**

# HALF REACTIONS

# HALF REACTIONS

All redox reactions may be divided into half-reactions. One half represents the oxidation, while the other is the reduction.

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

Oxidation: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$

Reduction: $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

Half-reactions are always written for a single mole of a substance.

# HALF REACTIONS

OXIDIZING STRENGTH

| Oxidizing strength | Oxidizing agent | | | Reducing agent | Reducing strength |
|---|---|---|---|---|---|
| Strong | $F_2$ | $+ 2e^-$ | $\rightarrow$ | $2F^-$ | Negligible |
| | $MnO_4^- + 8H^+$ | $+ 5e^-$ | $\rightarrow$ | $Mn^{2+} + 4H_2O$ | |
| | $Cl_2$ | $+ 2e^-$ | $\rightarrow$ | $2Cl^-$ | |
| | $Cr_2O_7^{2-} + 14H^+$ | $+ 6e^-$ | $\rightarrow$ | $2Cr^{3+} + 7H_2O$ | |
| | $O_2 + 4H^+$ | $+ 4e^-$ | $\rightarrow$ | $2H_2O$ | |
| Medium | $OCl^- + H_2O$ | $+ 2e^-$ | $\rightarrow$ | $Cl^- + OH^-$ | Weak |
| | $Ag^+$ | $+ e^-$ | $\rightarrow$ | $Ag$ | |
| | $Fe^{3+}$ | $+ e^-$ | $\rightarrow$ | $Fe^{2+}$ | |
| | $I_2$ | $+ 2e^-$ | $\rightarrow$ | $2I^-$ | |
| | $Cu^{2+}$ | $+ 2e^-$ | $\rightarrow$ | $Cu$ | |
| Weak | $Sn^{4+}$ | $+ 2e^-$ | $\rightarrow$ | $Sn^{2+}$ | Medium |
| | $2H^+$ | $+ 2e^-$ | $\rightarrow$ | $H_2$ | |
| | $Pb^{2+}$ | $+ 2e^-$ | $\rightarrow$ | $Pb$ | |
| | $Fe^{2+}$ | $+ 2e^-$ | $\rightarrow$ | $Fe$ | |
| Negligible | $Zn^{2+}$ | $+ 2e^-$ | $\rightarrow$ | $Zn$ | Strong |
| | $Mg^{2+}$ | $+ 2e^-$ | $\rightarrow$ | $Mg$ | |
| | $Na^+$ | $+ e^-$ | $\rightarrow$ | $Na$ | |
| | $Li^+$ | $+ e^-$ | $\rightarrow$ | $Li$ | |

REDUCING STRENGTH

Using the half-reactions table, one can predict whether a redox reaction will occur spontaneously.

An oxidizing agent (left column) will always spontaneously react with a reducing agent (right column) lower on the list.

**Table 20.1** Standard Reduction Potentials in Aqueous Solution at 25 °C*

| Reduction Half-Reaction | | $E°$ (V) |
|---|---|---|
| $F_2(g) + 2\,e^-$ | $\longrightarrow 2\,F^-(aq)$ | +2.87 |
| $H_2O_2(aq) + 2\,H^+(aq) + 2\,e^-$ | $\longrightarrow 2\,H_2O(\ell)$ | +1.77 |
| $PbO_2(s) + SO_4^{2-}(aq) + 4\,H^+(aq) + 2\,e^-$ | $\longrightarrow PbSO_4(s) + 2\,H_2O(\ell)$ | +1.685 |
| $MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^-$ | $\longrightarrow Mn^{2+}(aq) + 4\,H_2O(\ell)$ | +1.51 |
| $Au^{3+}(aq) + 3\,e^-$ | $\longrightarrow Au(s)$ | +1.50 |
| $Cl_2(g) + 2\,e^-$ | $\longrightarrow 2\,Cl^-(aq)$ | +1.36 |
| $Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^-$ | $\longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O\,(\ell)$ | +1.33 |
| $O_2(g) + 4\,H^+(aq) + 4\,e^-$ | $\longrightarrow 2\,H_2O(\ell)$ | +1.229 |
| $Br_2(\ell) + 2\,e^-$ | $\longrightarrow 2\,Br^-(aq)$ | +1.08 |
| $NO_3^-(aq) + 4\,H^+(aq) + 3\,e^-$ | $\longrightarrow NO(g) + 2\,H_2O(\ell)$ | +0.96 |
| $OCl^-(aq) + H_2O(\ell) + 2\,e^-$ | $\longrightarrow Cl^-(aq) + 2\,OH^-(aq)$ | +0.89 |
| $Hg^{2+}(aq) + 2\,e^-$ | $\longrightarrow Hg(\ell)$ | +0.855 |
| $Ag^+(aq) + e^-$ | $\longrightarrow Ag(s)$ | +0.799 |
| $Hg_2^{2+}(aq) + 2\,e^-$ | $\longrightarrow 2\,Hg(\ell)$ | +0.789 |
| $Fe^{3+}(aq) + e^-$ | $\longrightarrow Fe^{2+}(aq)$ | +0.771 |
| $I_2(s) + 2\,e^-$ | $\longrightarrow 2\,I^-(aq)$ | +0.535 |
| $O_2(g) + 2\,H_2O(\ell) + 4\,e^-$ | $\longrightarrow 4\,OH^-(aq)$ | +0.40 |
| $Cu^{2+}(aq) + 2\,e^-$ | $\longrightarrow Cu(s)$ | +0.337 |
| $Sn^{4+}(aq) + 2\,e^-$ | $\longrightarrow Sn^{2+}(aq)$ | +0.15 |
| $2\,H^+(aq) + 2\,e^-$ | $\longrightarrow H_2(g)$ | 0.00 |
| $Sn^{2+}(aq) + 2\,e^-$ | $\longrightarrow Sn(s)$ | −0.14 |
| $Ni^{2+}(aq) + 2\,e^-$ | $\longrightarrow Ni(s)$ | −0.25 |
| $V^{3+}(aq) + e^-$ | $\longrightarrow V^{2+}(aq)$ | −0.255 |
| $PbSO_4(s) + 2\,e^-$ | $\longrightarrow Pb(s) + SO_4^{2-}(aq)$ | −0.356 |
| $Cd^{2+}(aq) + 2\,e^-$ | $\longrightarrow Cd(s)$ | −0.40 |
| $Fe^{2+}(aq) + 2\,e^-$ | $\longrightarrow Fe(s)$ | −0.44 |
| $Zn^{2+}(aq) + 2\,e^-$ | $\longrightarrow Zn(s)$ | −0.763 |
| $2\,H_2O(\ell) + 2\,e^-$ | $\longrightarrow H_2(g) + 2\,OH^-(aq)$ | −0.8277 |
| $Al^{3+}(aq) + 3\,e^-$ | $\longrightarrow Al(s)$ | −1.66 |
| $Mg^{2+}(aq) + 2\,e^-$ | $\longrightarrow Mg(s)$ | −2.37 |
| $Na^+(aq) + e^-$ | $\longrightarrow Na(s)$ | −2.714 |
| $K^+(aq) + e^-$ | $\longrightarrow K(s)$ | −2.925 |
| $Li^+(aq) + e^-$ | $\longrightarrow Li(s)$ | −3.045 |

Increasing strength of oxidizing agents

Increasing strength of reducing agents

* In volts (V) versus the standard hydrogen electrode.

# HALF REACTIONS

**Standard Reduction Potentials at 25°C (298 K) for Many Common Half-Reactions**

| Half-Reaction | $\mathscr{E}°$ (V) | Half-Reaction | $\mathscr{E}°$ (V) |
|---|---|---|---|
| $F_2 + 2e^- \rightarrow 2F^-$ | 2.87 | $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ | 0.40 |
| $Ag^{2+} + e^- \rightarrow Ag^+$ | 1.99 | $Cu^{2+} + 2e^- \rightarrow Cu$ | 0.34 |
| $Co^{3+} + e^- \rightarrow Co^{2+}$ | 1.82 | $Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$ | 0.27 |
| $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ | 1.78 | $AgCl + e^- \rightarrow Ag + Cl^-$ | 0.22 |
| $Ce^{4+} + e^- \rightarrow Ce^{3+}$ | 1.70 | $SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$ | 0.20 |
| $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$ | 1.69 | $Cu^{2+} + e^- \rightarrow Cu^+$ | 0.16 |
| $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$ | 1.68 | $2H^+ + 2e^- \rightarrow H_2$ | 0.00 |
| $2e^- + 2H^+ + IO_4^- \rightarrow IO_3^- + H_2O$ | 1.60 | $Fe^{3+} + 3e^- \rightarrow Fe$ | −0.036 |
| $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ | 1.51 | $Pb^{2+} + 2e^- \rightarrow Pb$ | −0.13 |
| $Au^{3+} + 3e^- \rightarrow Au$ | 1.50 | $Sn^{2+} + 2e^- \rightarrow Sn$ | −0.14 |
| $PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$ | 1.46 | $Ni^{2+} + 2e^- \rightarrow Ni$ | −0.23 |
| $Cl_2 + 2e^- \rightarrow 2Cl^-$ | 1.36 | $PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$ | −0.35 |
| $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ | 1.33 | $Cd^{2+} + 2e^- \rightarrow Cd$ | −0.40 |
| $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ | 1.23 | $Fe^{2+} + 2e^- \rightarrow Fe$ | −0.44 |
| $MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$ | 1.21 | $Cr^{3+} + e^- \rightarrow Cr^{2+}$ | −0.50 |
| $IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$ | 1.20 | $Cr^{3+} + 3e^- \rightarrow Cr$ | −0.73 |
| $Br_2 + 2e^- \rightarrow 2Br^-$ | 1.09 | $Zn^{2+} + 2e^- \rightarrow Zn$ | −0.76 |
| $VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$ | 1.00 | $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ | −0.83 |
| $AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$ | 0.99 | $Mn^{2+} + 2e^- \rightarrow Mn$ | −1.18 |
| $NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$ | 0.96 | $Al^{3+} + 3e^- \rightarrow Al$ | −1.66 |
| $ClO_2 + e^- \rightarrow ClO_2^-$ | 0.954 | $H_2 + 2e^- \rightarrow 2H^-$ | −2.23 |
| $2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$ | 0.91 | $Mg^{2+} + 2e^- \rightarrow Mg$ | −2.37 |
| $Ag^+ + e^- \rightarrow Ag$ | 0.80 | $La^{3+} + 3e^- \rightarrow La$ | −2.37 |
| $Hg_2^{2+} + 2e^- \rightarrow 2Hg$ | 0.80 | $Na^+ + e^- \rightarrow Na$ | −2.71 |
| $Fe^{3+} + e^- \rightarrow Fe^{2+}$ | 0.77 | $Ca^{2+} + 2e^- \rightarrow Ca$ | −2.76 |
| $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ | 0.68 | $Ba^{2+} + 2e^- \rightarrow Ba$ | −2.90 |
| $MnO_4^- + e^- \rightarrow MnO_4^{2-}$ | 0.56 | $K^+ + e^- \rightarrow K$ | −2.92 |
| $I_2 + 2e^- \rightarrow 2I^-$ | 0.54 | $Li^+ + e^- \rightarrow Li$ | −3.05 |
| $Cu^+ + e^- \rightarrow Cu$ | 0.52 | | |

## Example #5

a) Will iodine be able to oxidize zinc metal to $Zn^{2+}$ ions?

Yes

b) Name an oxidizing agent that can oxidize $Br^-$ to $Br_2$, but cannot oxidize $Cl^-$ to $Cl_2$.

$O_2$, $MnO_2$, $Cr_2O_7^{2-}$

# HALF REACTIONS

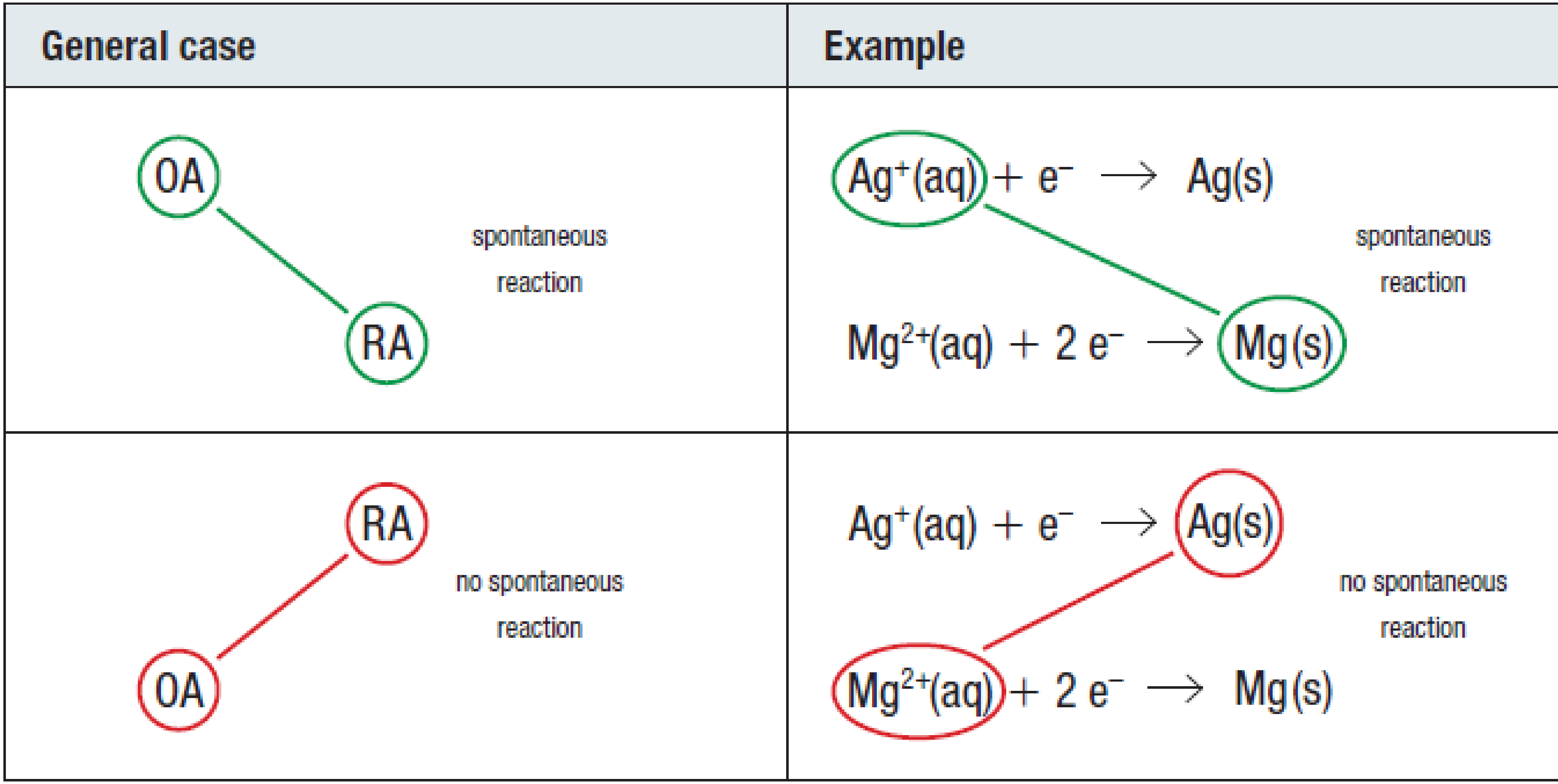


**Figure 2** When an oxidizing agent (OA) is above the reducing agent (RA) on the redox table, a spontaneous reaction occurs. But when an oxidizing agent is below the reducing agent, no spontaneous reaction occurs. As an example, when $Ag^{+}(aq)$ is the oxidizing agent and Mg(s) is the reducing agent, a reaction occurs.