Redox Reactions

NOTE: Look in textbook for pages on Oxidation Number and Redox that are prior to Electrochemistry Chapter. Read and Review that material.

Oxidation Number (ox nu)

Charges are either real or “imaginary”
Positive or negative ox nu indicates unequal sharing of electrons in covalent compounds (molecules) or ions

Example: oxidation numbers are
LiF Li (+1) F (-1) real charges Li⁺ F⁻
HF H (+1) F (-1) “imaginary” charges
meaning F pulls electron toward it and away from H

Ox nu. provides a way of keeping track of transfer of electrons or unequal sharing of electrons

More electronegative atom in bonded pair has the negative oxidation number as if it has an extra electron F is more electronegative than H

However, if atoms are the same as in pure element H₂ or Cu
H₂ ox nu are H (0) H (0) because there is equal sharing of e
Cu ox nu is Cu(0) since pure element and no unequal sharing of e

Note: The electronegative (EN) trend of the periodic table is greater EN as you go up and to the right on the periodic table with fluorine having the highest EN. F is most electronegative and O is next most EN. Ignore the noble gases completely.

Consider H to be where P is on periodic table (H same EN as P)
Rules to assign ox nu:

1. Sum of oxidation numbers add up to charge of species (ion or molecule)

   ex. \( \text{H}_2\text{S} = 2(\text{H}) + (\text{S}) = 0 \quad \text{Na}^+ = (+1) \quad \text{Al} = (0) \quad \text{Al}^{3+} = (+3) \)

2. Neutral uncombined atom or atom in pure element is assigned 0

   ex. \( \text{Cl}_2 \) (0) and \( \text{Na} \) (0)

   but in atom ion with actual charge that is the oxidation number

   ex. \( \text{NaCl} \) made of ions \( \text{Na}^+ \) and \( \text{Cl}^- \)

   then ox nu \( \text{Na} \) (+1) and \( \text{Cl} \) (-1)

3. Oxidation number of more electronegative is negative and equal to
   common charge of monatomic ion

   ex. \( \text{PCl}_3 \) where \( (\text{P}) = (+3) \) and \( (\text{Cl}) = (-1) \)

   since Cl is more electronegative and its charge is -1

Order of Selection (when dealing with a compound)

In pure element ox nu is 0

Examples: \( \text{Na} \quad \text{F}_2 \quad \text{H}_2 \quad \text{Br}_2 \quad \text{Al} \) all have ox nu =0

(no e transfer and no unequal sharing)

In charged (polyatomic ion) or neutral compound with two or more
different elements use:

1. First Always have
   
   Group 1 or IA = (+1)
   
   Group 2 or IIA = (+2)
   
   F = -1

   Note these ox nu. are in compounds. In pure element would be 0

2. Second Usually have

   O = -2  exception: \( \text{OF}_2 \) where O = (+2) since F = (-1)

   H = +1  exception: metal hydride \( \text{NaH} \) since Na = (+1) and H = (-1)

3. Remaining All other atoms next
Examples of determining oxidation numbers:

Cr$_2$O$_7^{2-}$ dichromate  USE Ox for oxygen O so not confused with zero 0
2(Cr) + 7(Ox) = -2
2(Cr) + 7(-2) = -2
2 Cr = 12
Cr = +6  oxidation number of Cr

CaH$_2$ calcium hydride
1(+2) + 2(H) = 0
2H = 0  - 2
H = -1  oxidation number of H

ClO$_4^-$ perchlorate
1(Cl) + 4(-2) = -1
Cl = -1 + 8
Cl = 7  oxidation number of Cl

H$_2$SO$_4$
2(+1) + 1(S) + 4(-2) = 0
S = 6  oxidation number of S

S
Pure element so S = (0)

Range of oxidation number possible for an atom

Highest oxidation number for family is:
  Roman numeral group number
  or second digit of modern group number

Lowest oxidation number for a family is charge of monatomic ion

  Example sulfur  group VI A or 16 so highest is  +6
  And lowest ox nu is charge on S  -2

  Sodium in group IA or 1 so highest is +1
  and charge is +1  so lowest and highest same  +1

Again these rules are all for compounds.
If you have just a piece of pure sulfur or sodium then pure element and
S  ox nu is (0)  Na  ox nu is (0)
Redox Reactions are **Reduction** oxidation together

Oxidation numbers provide a way to follow changes in Redox reactions

**Reduction**: atom decreases oxidation number

**Oxidation**: atom increases oxidation number

Reduction is gain of electrons (real or “imaginary”)

gain of e make ox nu decrease since gain electrons with -1 charge

**Oxidation** is loss of electrons

Electron change can be real or “imaginary”

Examples:

Combustion:

S (0) + O_2 (0) → SO_2 where S = (+4) and O = (-2)

Sulfur Oxidized Oxygen Reduced

Reducing agent Oxidizing agent

(reductant) (oxidant)

Note in above S went from 0 to +4 so increase in ox nu and

and two O went from 0 to -2 so decrease in ox nu

And total increase +4 balances total decrease 2 (-2) = -4

**In Redox reaction: increase in ox nu cancels out decrease in ox nu**

Combination:

2Na (s) + Cl_2(g) → 2NaCl(s) where Na = +1 and Cl = -1

so actual transfer of electrons

Write as half reactions (show electrons)

Oxidation 2 (Na → Na^+ + e-)

2 Na → 2 Na^+ + 2e- Loss of 2e

Reduction 2e- + Cl_2 → 2Cl- Gain of 2e

Reduction Oxidation occurs together to make Redox reaction

no net change in oxidation number in a reaction (reactants → products)
Balance Redox Equation with Ion-Electron Method
or (Half-Reaction Method)

Useful for ions and molecules reacting in water

Rules:
1. Write two Half Reactions and Balance both for
   a. the number of the key atom (the one changing ox nu)
   b. and change in oxidation number with electrons
2. Add Half reactions so electrons cancel
3. Balance charge with base (OH⁻) and acid (H⁺)
4. Balance O with H₂O
5. Check that there is no net change in charge or number of atoms

Summary:
Steps 1 and 2 divide the reaction into half reactions,
then balance ox nu change with e- and combine the reactions
Step 3 Balance charge with H⁺ (in acid) or OH⁻ (in base)
Step 4 Balance oxygen atoms with H₂O
Example:

Balance below using Half-Reaction Method in acid (H⁺) solution

\[ \text{MnO}_4^- \quad + \quad \text{Fe}^{2+} \quad \rightarrow \quad \text{Mn}^{2+} \quad + \quad \text{Fe}^{3+} \]

1) Write Half-Reactions and balance ox nu change with electrons e-

\[ 5e^- + \text{MnO}_4^- \rightarrow \text{Mn}^{2+} \quad \text{Mn} \quad 5e^- + (+7) \rightarrow (2) \]

\[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^- \quad \text{Fe} \quad (2) \rightarrow (3) + e^- \]

2) Add half reactions to cancel electrons (multiple 2\text{nd} half reaction by 5)

\[ 5e^- + \text{MnO}_4^- \rightarrow \text{Mn}^{2+} \]

\[ 5 \text{Fe}^{2+} \rightarrow 5 \text{Fe}^{3+} + 5e^- \]

\[ \text{MnO}_4^- + 5 \text{Fe}^{2+} \rightarrow 5 \text{Fe}^{3+} + \text{Mn}^{2+} \]

3) Balance charge with H⁺ if in acid

\[ -1 + +10 \rightarrow +15 + +2 \]

\[ 8\text{H}^+ + (+9) \rightarrow (+17) \]

4) Balance O with H₂O

\[ 4 \text{Ox} \rightarrow 0 \text{Ox} + 4\text{H}_2\text{O} \]

5) Write out reaction, make sure no change in atoms or charge from left to right side

\[ 8\text{H}^+ + \text{MnO}_4^- + 5\text{Fe}^{2+} \rightarrow 5\text{Fe}^{3+} + \text{Mn}^{2+} + 4\text{H}_2\text{O} \]

\text{MnO}_4^- \text{ is permagnate ion} \quad \text{and} \quad \text{Mn}^{2+} \text{ is manganese(II) ion}
Example of Half-Reaction Method in acidic (H\(^+\)) solution

1) Identify oxidation numbers in half reactions and make sure number of atoms that change ox nu is same on both sides

\(2\text{ Cr going to } 2\text{ Cr} \quad \text{and } 2\text{ Cl}^- \text{ going to Cl}_2\)

Note: Cr oxidation number is (+6) and goes to (+3)

\[
\begin{align*}
\text{Cr}_2\text{O}_7^{2-} & \quad + \quad \text{Cl}^- & \quad \rightarrow \quad \text{Cr}^{3+} & \quad + \quad \text{Cl}_2 \\

\text{Cr}_2\text{O}_7^{2-} & \quad + \quad 6\text{e}^- & \quad \rightarrow \quad 2\text{Cr}^{3+} & \quad + \quad 2\text{Cl}^- & \quad (12 + 6\text{e}^- \rightarrow 6) \\
3 & \quad (2\text{Cl}^- & \quad \rightarrow \quad \text{Cl}_2 & \quad + \quad 2\text{e}^-) & \quad 3 \quad (-2 \rightarrow 0 + 2\text{e}^-)
\end{align*}
\]

2) Multiple and add to cancel e-

\[
\begin{align*}
\text{Cr}_2\text{O}_7^{2-} & \quad + \quad 6\text{Cl}^- & \quad \rightarrow \quad 2\text{Cr}^{3+} & \quad + \quad 3\text{Cl}_2 \\
6 & \quad \text{Cl}^- & \quad \rightarrow \quad 3\text{Cl}_2 & \quad + \quad 6\text{e}^- \\
\hline
\text{Cr}_2\text{O}_7^{2-} & \quad + \quad 6\text{Cl}^- & \quad \rightarrow \quad 2\text{Cr}^{3+} & \quad + \quad 3\text{Cl}_2
\end{align*}
\]

3) Balance charge with H\(^+\) in acid or OH\(^-\) in base

\[
14\text{H}^+ & \quad + \quad -2 & \quad + \quad -6 \quad \rightarrow \quad +6
\]

4) Balance O with H\(_2\)O

\[
7 \quad \text{Ox} & \quad \rightarrow \quad 0 \quad \text{Ox} & \quad + \quad 7\text{H}_2\text{O}
\]

\[
\begin{align*}
14\text{H}^+ & \quad + \quad \text{Cr}_2\text{O}_7^{2-} & \quad + \quad 6\text{Cl}^- & \quad \rightarrow \quad 2\text{Cr}^{3+} & \quad + \quad 3\text{Cl}_2 & \quad + \quad 7\text{H}_2\text{O}
\end{align*}
\]

Cr\(_2\)O\(_7^{2-}\) is dichromate ion and Cr\(^{3+}\) is chromium(III) ion
Oxidation Number Method (Oxidation State Method)
another method when you do not divide into half reactions

Charge and mass both must be balanced

1. Determine oxidation number of atoms to see which ones are changing
2. Put in coefficients so no net change in oxidation number
3. Balance remaining atoms that are not involved in change of ox nu

Example: Given reaction below balance it

1. \( \text{HNO}_3 + \text{H}_2\text{S} \rightarrow \text{NO} + \text{S} + \text{H}_2\text{O} \)
   
   \[
   \begin{align*}
   \text{N} & = 5 & \text{S} & = -2 \\
   \text{N} & \rightarrow 2 & \Delta & = -3 \text{ reduction} \\
   \text{S} & \rightarrow 0 & \Delta & = +2 \text{ oxidation}
   \end{align*}
   \]

2. Multiply N by 2 and S by 3 (cross multiple)
   
   \( 2\text{HNO}_3 + 3\text{H}_2\text{S} \rightarrow 2\text{NO} + 3\text{S} + \text{H}_2\text{O} \)

3. Balance O in \( \text{H}_2\text{O} \)
   
   \[
   \begin{align*}
   6(\text{Ox}) & \rightarrow 2(\text{Ox}) + 4\text{H}_2\text{O}
   \end{align*}
   \]

Write final reaction and make sure balanced
(same number of atoms on left and right side)

\( 2\text{HNO}_3 + 3\text{H}_2\text{S} \rightarrow 2\text{NO} + 3\text{S} + 4\text{H}_2\text{O} \)
More examples of Redox reactions:

Combustion of hydrogen and oxygen to produce water:

\[
2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g}) + \text{heat}
\]

notice that 4 H atoms go from (0) to (1) \( \Delta \text{ox nu} = 4(1) = +4 \)

and 2 O atoms goes from (0) to (-2) \( \Delta \text{ox nu} = 2(-2) = -4 \)

http://www.youtube.com/watch?v=-R8fmSbmXso

Thermite reaction:

\[
\text{Fe}_2\text{O}_3 + 2 \text{Al} \rightarrow \text{Al}_2\text{O}_3 + 2 \text{Fe} + \text{heat}
\]

2 Fe atoms go from (3) to (0) \( \Delta \text{ox nu} = 2(-3) = -6 \)

2 Al atoms go from (0) to (3) \( \Delta \text{ox nu} = 2(3) = +6 \)

http://en.wikipedia.org/wiki/Thermite

http://www.youtube.com/watch?v=a8XSsSmvdEK4
EXTRA

Example half reaction method in base
with one type of atom that is both reduced and oxidized

Balance below in base \( \text{Br}_2 \rightarrow \text{BrO}_3^- + \text{Br}^- \)

So two half-reactions but involve same type of atom so two half reactions

1) Identify oxidation numbers in half reactions and
make sure number of atoms that change ox nu is same on both sides

\[
\begin{align*}
\text{Br}_2 & \rightarrow 2\text{BrO}_3^- & (0) & \rightarrow 2(+5) + 10\text{e}^- \\
\text{Br}_2 & \rightarrow 2\text{Br}^- & 2\text{e}^- & + 2(0) \rightarrow 2(-1)
\end{align*}
\]

So then

\[
\begin{align*}
\text{Br}_2 & \rightarrow 2\text{BrO}_3^- + 10\text{e}^- \\
2\text{e}^- & + \text{Br}_2 \rightarrow 2\text{Br}^- 
\end{align*}
\]

2) Multiple and add to cancel e-

\[
\begin{align*}
\text{Br}_2 & \rightarrow 2\text{BrO}_3^- + 10\text{e}^- \\
5(2\text{e}^- & + \text{Br}_2 \rightarrow 2\text{Br}^- ) \\
\text{Br}_2 + 5\text{Br}_2 & \rightarrow 2\text{BrO}_3^- + 10\text{Br}^- 
\end{align*}
\]

3) Balance charge with \( \text{H}^+ \) in acid or \( \text{OH}^- \) in base

\[
\begin{align*}
\text{Br}_2 + 5\text{Br}_2 & \rightarrow 2\text{BrO}_3^- + 10\text{Br}^- \\
0 & \rightarrow 2(-1) + 10(-1) \text{ so } 12\text{OH}^- + 0 \rightarrow -12
\end{align*}
\]

4) Balance O with \( \text{H}_2\text{O} \)

\[
\begin{align*}
6\text{H}_2\text{O} & + 0 \text{(Ox)} \rightarrow 6 \text{(Ox)} \\
\text{so } 6\text{H}_2\text{O} & + 12 \text{OH}^- + 6\text{Br}_2 \rightarrow 2\text{BrO}_3^- + 10\text{Br}^- \\
\text{or can simplify (divide by 2) and write as}
\end{align*}
\]

\[
\begin{align*}
3\text{H}_2\text{O} & + 6 \text{OH}^- + 3\text{Br}_2 \rightarrow \text{BrO}_3^- + 5 \text{Br}^-
\end{align*}
\]
Example of Half-Reaction Method in basic (OH\textsuperscript{−}) solution

Given \( \text{MnO}_4^- + \text{N}_2\text{H}_4 \rightarrow \text{MnO}_2 + \text{N}_2 \) balance in basic solution

1) Identify oxidation numbers in half reactions and make sure number of atoms that change ox nu is same on both sides

\[ \text{MnO}_4^- \rightarrow \text{MnO}_2 \]

\[ \text{N}_2\text{H}_4 \rightarrow \text{N}_2 \]

\text{Mn} \quad \text{ox nu} \quad 7 \rightarrow +4 \quad \Delta \text{ox nu} = 1 \ (-3) = -3

\text{2 N} \quad \text{ox nu} \quad -2 \rightarrow 0 \quad \Delta \text{ox nu} = 2 \ (+2) = +4

\[ 3 \text{ e}^- + \text{MnO}_4^- \rightarrow \text{MnO}_2 \]

\[ \text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 4 \text{ e}^- \]

2) Multiple and add to cancel e-

\[ 4 \text{ MnO}_4^- + 3 \text{ N}_2\text{H}_4 \rightarrow 4 \text{ MnO}_2 + 3 \text{ N}_2 \]

3) Balance charge with \( \text{H}^+ \) in acid or \( \text{OH}^- \) in base

\[ \text{add OH}^- \text{ for charge} \quad -4 \rightarrow +4\text{OH}^- \]

4) Balance O with \( \text{H}_2\text{O} \)

\[ \text{balance oxygen with } \text{H}_2\text{O} \quad 16 \rightarrow 12 + 4\text{H}_2\text{O} \]

so the result is:

\[ 4 \text{ MnO}_4^- + 3 \text{ N}_2\text{H}_4 \rightarrow 4 \text{ MnO}_2 + 3 \text{ N}_2 + 4\text{OH}^- + 4\text{H}_2\text{O} \]