Redox Reactions

Oxidation Numbers

Charges are either real or "imaginary" (indicating 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 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

Rules to assign ox nu:

1. Sum of oxidation numbers add up to charge of species (ion or molecule)
   ex. H_2S = 2(H) + (S) = 0 Na^+ = (+1)   Al = (0) Al^{3+} = (+3)

2. Neutral uncombined atom or atom in pure element is assigned 0
   ex. Cl_2 (0) and Na (0)
   but in ion with actual charge that is the oxidation number
   for example NaCl made of ions Cl^- and Na^+ then   Cl (-1)   Na   (+1)

3. Oxidation number of more electronegative is negative and equal to common charge of monatomic ion
   ex. PCl_3 where (P) = (+3) and (Cl) = (-1)
   since Cl is more electronegative and its charge is -1

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.
Ignore the noble gases completely.
Consider H to be where P is on periodic table (H same EN as P)

<u>Order of Selection (when dealing with a compound)</u>

In pure element ox nu is 0   Examples: Na F_2 H_2 Br_2 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:

First 1. 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

Second 2. Usually have
O = -2   Exception: OF_2 where O = (+2) since F = (-1)
H = +1   Exception: metal hydride NaH since Na = (+1) and H= -1

Rest 3. All other atoms next

Examples of determining oxidation numbers:

$Cr_2O_7^{2-}$ 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_2SO_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 1**6** so highest is +6
And lowest ox nu is charge on S -2

Sodium in group IA 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 sodium metal then pure element and so ox nu is (0) pure sulfur is ox nu (0) etc.

These oxidation umbers provide a way to follow changes in Redox reactions

Redox Reactions

Reduction: atom decreases oxidation number
Oxidation: atom increases oxidation number

Reduction is gain of electrons (real or "imaginary")
gain make ox nu decrease since gaining negative 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
While 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-) Loss of 2e-
Reduction 2e- + Cl_2 → 2Cl- Gain of 2e-

Reduction **Ox**idation occurs together **Redox** so no net change in oxidation number in a reaction (reactants → products)

Balance Redox Equation with Ion-Electron Method (Half-Reaction Method)
Use for ions

Rules
1. Write Half Reactions and Balance both
    a. the number of the significant atom (the one changing oxidation number)
    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 H_2O

5. Check that there is no net change in charge or number of atoms

Summary:
Steps 1-2 reaction is divided, then balance ox nu and combine the reactions
Step 3 Balance charge
Step 4 Balance oxygen atoms

Example:

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

MnO_4^- + Fe^{2+} → Mn^{2+} + Fe^{3+}

1) Write Half-Reactions and balance

5e- + MnO_4^- → Mn^{2+} Mn 5e- + (+7) → (2)
(Fe^{2+} → Fe^{3+} + e-) Fe (2) → (3) + e-

2) Add half reactions to cancel electrons (multiple 2nd half reaction by 5)

MnO_4^- + $5Fe^{2+}$ → $5Fe^{3+}$ + Mn^{2+}

3) Balance charge with H^+ if in acid

-1 + +10 → +15 + +2
$8H^+$ + +9 → +17

4) Balance O with H_2O

4 Ox → 0 Ox + **$4H_2O$**

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

$8H^+$ + MnO_4^- + $5Fe^{2+}$ → $5Fe^{3+}$ + Mn^{2+} + $4H_2O$

MnO_4^- is permagnate ion and Mn^{2+} 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 Cr and 2 Cl

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

$Cr_2O_7^{2-}$ + Cl^- → Cr^{3+} + Cl_2

$Cr_2O_7^{2-}$ + **6e-** → $2Cr^{3+}$ 2Cr (12 + **6e-** → 6)
3($2Cl^-$ → Cl_2 + **2e-**) 2Cl 3 (-2 → 0 + **2e-**)

2) Multiple and add to cancel e-

$Cr_2O_7^{2-}$ + $6Cl^-$ → $2Cr^{3+}$ + $3Cl_2$

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

$14H^+$ + -2 + -6 → +6

4) Balance O with H_2O

7 Ox → 0 Ox + **$7H_2O$**

$Cr_2O_7^{2-}$ is dichromate ion and Cr^{3+} is chromium(III) ion

Oxidation Number Method (Oxidation State Method)
another method when 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 oxidation number

Example: Given reaction below balance it

1. $HNO_3 + H_2S \rightarrow NO + S + H_2O$

N = 5 S = -2 → N = 2 S = 0

N 5→2 $\Delta = -3$ reduction
S -2 → 0 $\Delta = +2$ oxidation

2. Multiply N by 2 and S by 3 (cross multiple)

$2HNO_3 + 3H_2S \rightarrow 2NO + 3S + H_2O$

3. Balance O in H_2O

6(Ox) → 2(Ox) + **$4H_2O$**

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

$2HNO_3 + 3H_2S \rightarrow 2NO + 3S + 4H_2O$

EXTRA Example half reaction method

Balance below in base

$Br_2 \rightarrow BrO_3^- + Br^-$

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

$Br_2 \rightarrow 2BrO_3^-$ (0) $\rightarrow$ 2(+5) + 10e-

$Br_2 \rightarrow 2Br^-$ 2e- + 2 (0) $\rightarrow$ 2 (-1)

So then

$Br_2 \rightarrow 2BrO_3^- + 10e^-$

$2e^- + Br_2 \rightarrow 2Br^-$

2) Multiple and add to cancel e-

$Br_2 \rightarrow 2BrO_3^- + 10e^-$

$5\ (2e^- + Br_2 \rightarrow 2Br^-)$

$Br_2 + 5Br_2 \rightarrow 2BrO_3^- + 10Br^-$

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

$Br_2 + 5Br_2 \rightarrow 2BrO_3^- + 10Br^-$ 0 $\rightarrow$ 2(-1) +10(-1) **so** $\mathbf{12OH^-}$ + 0 $\rightarrow$ -12

+ 12 $\mathbf{OH^-}$

4) Balance O with H_2O

$\mathbf{6\ H_2O}$ + 0 (Ox) $\rightarrow$ 6 (Ox)

so $\mathbf{6\ H_2O} + 12\ OH^- + 6\ Br_2 \rightarrow 2BrO_3^- + 10Br^-$

or can simplify (divide by 2) and write as

$3\ H_2O + 6\ OH^- + 3\ Br_2 \rightarrow BrO_3^- + 5\ Br^-$