Assigning Oxidation Numbers

Oxidation numbers are hypothetical charges given to each atom in any substance for the purpose of keeping track of transfer of electrons. Any oxidation-reduction reaction must involve a change of oxidation number in at least two of the elements. If there is not changes, the reaction is not redox. Note: Oxidation numbers often will not be the charge predicted from the Periodic Table.

LEARN THESE RULES IN ORDER!
1. Oxid # of any free element is zero.
   e.g. H in H₂, P in P₄ are assigned zero.
2. Oxid # of a simple monatomic ion is the charge of the ion.
   e.g. In MgCl₂, Mg is +2, Cl is –1.
   e.g. In SnS, Sn is +2, S is –2.
3. In its compounds F is assigned –1.
4. In its compound H is +1 unless it is bonded to a metal (then H is –1, as in hydride H⁻).
   e.g. In HCl, H is +1 and Cl is –1.
   e.g. In MgH₂, Mg is +2 and H is –1.
5. In its compounds, O is –2 unless it is a peroxide (then O is –1).
   e.g. In MgO, Mg is +2 and O is –2.
   e.g. In hydrogen peroxide (H₂O₂), H is +1 and O is –1.
6. Oxid # of others are generally calculated from knowing that the sum of all the charges must add up to the charge of the substance.
   e.g. In HClO, sum of charges = 0. Assign oxid # to H and O based on rules & calculate for Cl.
     +1 ? –2
     First we assign H to be +1, O to be –2. Cl is calculated to be +1 in order for the sum to be zero.
     It is NOT –1 as you might expect. This is because Cl in HClO is NOT the chloride ion Cl⁻.
   e.g. In ClO₂⁻, we see that sum of charges = –1. We know O is –2. What is Cl?
     ? –2
     O is assigned –2 each. Two O would give a charge of –4. Cl must be +3 in order for the net charge to be –1.
   e.g. In Cl₂O, sum of charges = 0. Assign O to be –2, so two Cl would be +2, so EACH Cl would be +1. Remember oxid # is defined to be for EACH atom.
   e.g. In Ba(ClO₄)₂, first separate them into ions: Ba²⁺ and ClO₄⁻.
     Ba is +2, O is –2. What is Cl? You can calculate from ClO₄⁻ and come up with +7.
     Or, you can calculate from Ba(ClO₄)₂ thus: charge = +2 ? –16
       Ba (ClO₄)₂
     oxid # = +2 ? –2
     Ba is +2, O is –2 each, but there are 8 O’s, so total charge is –16.
     +2 + ? –16 = 0 Ans is +14, but this is for two Cl, so each Cl must be (+14)/2 = +7
     Ans. Ba = +2, O = –2, Cl = +7

In these 4 examples, you see that Cl has different oxidation numbers, none of which is –1!
Give the oxidation numbers for the element specified:

1. P in PO$_3^-$: P = ___
2. N in N$_2$H$_4$: N = ___
3. Cr in K$_2$Cr$_2$O$_7$: Cr = ___
4. N in Ca(NO$_3$)$_2$: N = ___

Ans. +3, -2, +6, +5

First of all, when determining oxidation numbers, ignore the coefficients. Remember that coefficients are not part of the formulas. They only tell you how many moles of present, not WHAT is present. (Remember we don’t include the coefficients when we calculate the molar masses, right!?)

Do the following in the reaction below:
1. Assign oxidation numbers to every element.
2. Determine which element is oxidized (oxidation number is increased).
3. Is this element losing or gaining electrons? How many electrons are involved?
4. Determine which element is reduced (oxidation number is decreased).
5. Is this element losing or gaining electrons? How many electrons are involved?
6. Identify how many electrons are being transferred in the balanced equation.
7. Draw an arrow to show where the electrons are coming from and where they are going.
8. Identify which the oxidizing and reducing agents are.

\[
2\text{PbS} + 3\text{O}_2 \rightarrow 2\text{PbO} + 2\text{SO}_2
\]

Ans. S is oxidized. Its oxidation number increased from -2 to +4. Each loses 6 e$^-$. In the balanced equation there are 2 S, so a total of 2x6=12 e$^-$ are lost.

O is reduced. Its oxidation number decreased from zero to -2. Each gains 2 e$^-$. In the balanced equation, there are 6 oxygen, so a total of 6x2=12 e$^-$ are gained.

PbS is the reducing agent because it is oxidized. O$_2$ is the oxidizing agent because it is reduced.

\[
2\text{PbS} + 3\text{O}_2 \rightarrow 2\text{PbO} + 2\text{SO}_2
\]

Arrow shows transfer of electrons.