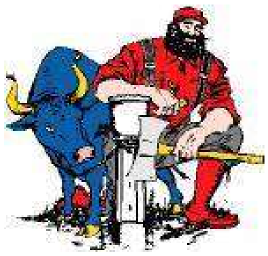
C04.4 and C19.1 Oxidation-Reduction Reactions



Red Ox and Blue Ox (Apologies to the Monty Python)

He's a Lumberjack and he works all day.
He's got the Blue Ox, Babe, to help on those tough days.

You're an AP Chem Student and you study till May.
You've got the Red Ox to help balance reactions in an electron way.

4.04 Oxidation-Reduction Reactions

Lightly read through the section, and then focus on the summary which explains in detail what is required for AP Chemistry.

Oxidation reduction reactions involve changes in the control of electrons in covalent bonds. The first step in learning how to work with oxidation-reduction chemistry is to determine the level of control of electrons in bonds which is called the oxidation state. The oxidation state is described by assigning an oxidation number to each element in a reaction.

Typically, the oxidation number is shown above the element

e.g. The formula of sodium oxide, Na_2O, and nitrate, NO_3^-, with oxidation numbers are written as:

$$\overset{+1}{Na}_2\overset{-2}{O} \qquad \left(\overset{+5}{N}\overset{-2}{O}_3\right)^-$$

The oxidation number is for the individual atom. For Na_2O, each of the two sodium atoms has an oxidation number of +1 and the oxygen atom has an oxidation number of -2. For NO_3^-, the nitrogen has an oxidation umber of +5 and each oxygen atom in nitrate has an oxidation number of -2.

The total "oxidation number value" in each element in the substance is usually shown under the element. In a neutral compound, the sum of the oxidation number values is 0. In a polyatomic ion, the sum of the oxidation number charges is equal to the charge of the ion.

$$\underbrace{\underset{+2}{\overset{+1}{Na_2}}\ \underset{-2}{\overset{-2}{O}}}_{0} \qquad \underbrace{\left(\underset{+5}{\overset{+5}{N}}\ \underset{-6}{\overset{-2}{O_3}}\right)^-}_{-1}$$

Oxidation numbers are treated as numbers rather than charges. The sign precedes the number as opposed to the number-then-sign order which is used to depict charges.

AP Chemistry exam questions may ask for the oxidation number of a substance.

Here are the rules for determining the oxidation state number of atoms in reactions.
The rules are logical if you understand electronegativity and remember your atomic and polyatomic ion charges.

	Oxidation Number Rules	Examples	
1.	Elements and molecules containing only one element have an oxidation number of zero.	Ti F_2 S_8	0 0 0
2.	Monatomic ions have an oxidation number equal to the charge on the ion.	Cl^- Mg^{2+}	-1 +2
3.	In compounds: All alkali metals have an oxidation number of +1. All alkaline earth metals have an oxidation number of +2. Aluminum is always +3.	Li in LiCl Mg in $MgCl_2$ Al in Al_2O_3	+1 +2 +3
4.	In compounds : Fluorine is always assigned an oxidation number of -1. Halogens often have an oxidation number of -1 , but this may be changed if they are bonded to an atom with greater electronegativity.	F in NaF Cl in $MgCl_2$	-1 -1
5.	In compounds : Oxygen is assigned an oxidation number of -2 Except… When oxygen is a peroxide and has an oxidation number of -1 (You will be told that the compound is a peroxide rather than an oxide). When oxygen is in a compound with fluorine where it will have a positive oxidation number that depends on the number of fluorine atoms	O in Na_2O O in Na_2O_2 O in OF_2	-2 -1 +2
6.	In compounds : Hydrogen has an oxidation number of +1 Except when it's in a binary compound with metals as a hydride in which case the oxidation number of hydrogen is -1.	H in HNO_3 H in NaH	+1 -1
7.	In a neutral molecule, the sum of oxidation numbers is 0.	$CuCl_2$	0
8.	In a polyatomic ion, the sum of oxidation numbers is equal to the charge of the ion.	$H_2PO_4^-$ SO_3^{2-}	-1 -2

Practice will make you proficient in oxidation numbers.

What is the oxidation number for each element in the following compounds[1]?

1. SO_2 2. CO_3^{2-} 3. K_2SO_4 4. P_2O_5

5. I_2 6. NH_4^+ 7. $Na_2Cr_2O_7$ 8. $Ca(OH)_2$

[1] Answers are on the last page.

Oxidation and Reduction Reactions

Oxidation reduction reactions have changes in oxidation numbers. An element's change in oxidation number indicates gain or loss of electrons.

Oxidation reduction reaction:

$$\overset{0}{H_2} + \overset{0}{Cl_2} \rightarrow 2\,\overset{+1-1}{HCl}$$

Not an oxidation reduction reaction:

$$\overset{+1-1}{HCl} + \overset{+1-2+1}{KOH} \rightarrow \overset{+1-2}{H_2O} + \overset{+1-1}{KCl}$$

Oxidation and Reduction Reactions involve loss and gain of electrons in a chemical reaction.

LEO the Lion goes GER is the common mnemonic used for Red Ox

Oxidation - Electrons are *lost* (**L**oss of **E**lectrons, **O**xidation).
Reduction - Electrons are *gained* (**G**ain of **E**lectrons, **R**eduction)

<table>
<tr>
<td>Oxidized substance (loss of electrons)

The oxidation number of the oxidized substance increases in the reaction because of the loss of negatively charged electrons.

e.g. -2 to -1 or +3 to +4

$\overset{0}{H_2} + Cl_2 \rightarrow 2\,\overset{+1}{H}Cl$

Hydrogen is oxidized from 0 to +1.

The oxidation half-reaction is written as :

$H_2 \rightarrow 2\,H^+ + 2e^-$</td>
<td>Reduced substance (gain of electrons)

The oxidation number of the reduced substance decreases in the reaction because of the gain of negatively charged electrons.

e.g. -1 to -2 or +4 to +3

$H_2 + \overset{0}{Cl_2} \rightarrow 2\,H\overset{-1}{Cl}$

Chlorine is reduced from 0 to -1.

The oxidation half-reaction is written as :

$Cl_2 + 2e^- \rightarrow 2\,Cl^-$</td>
</tr>
<tr>
<td>Reducing agent
A substance that undergoes oxidation (LEO) gives its electrons to another substance.
The substance that undergoes oxidation causes the reduction of another substance, and therefore is called a "reducing agent."</td>
<td>Oxidizing Agent
A substance that undergoes reduction (GER) takes electrons from another substance.
The substance that undergoes reduction causes the oxidation of another substance, and therefore is called an "oxidizing agent."</td>
</tr>
<tr>
<td colspan="2">Note: The terms Oxidizing Agent and Reducing Agent are not used on the AP exam.
However, they are used on the CLEP and college classes.

"Agent" terminology is used extensively in college chemistry. Here's at typical question.

What is the oxidizing agent in the reaction: $H_2 + Cl_2 \rightarrow 2\,HCl$?

The "same" question on an AP exam would be: Which substance in the reaction undergoes reduction? [2]</td>
</tr>
<tr>
<td colspan="2">Hazard warning placards use the term "Oxidizing agent" to warn of materials that gain electrons, that is reduce, such as elemental oxygen, elemental halogens, chlorates, nitrates, and peroxides.
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</table>

[2] Chlorine is the oxidizing agent and is the substance that reduces from 0 to -1.

Common Oxidation numbers of oxidizing agents, substances that reduce.

Oxides of Cr, Mn, and N reduce from high oxidation numbers and are used in many oxidation-reduction problems.

Memorizing the oxidation numbers of these **four common oxidizing agents** will save you valuable time in calculating complicated redox numbers.

Nitrogen in Nitrate	NO_3^-	N +5
Chromium in Chromate	CrO_4^{2-}	Cr +6
Chromium in Dichromate	$Cr_2O_7^{2-}$	Cr +6
Manganese in Permanganate	MnO_4^-	Mn +7

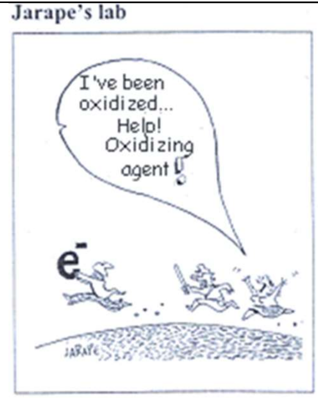
These compounds reduce from their large positive oxidation numbers, taking electrons from other substances to lower their own oxidation numbers and are labelled with warnings as oxidizing agents.

Practice will make you proficient in identifying oxidation and reduction in reactions.
Answers are on the last page.

In each of the following reactions, identify which reactant is oxidized and which is reduced.

1. $H_2(g) + Cl_2(g) \rightarrow 2\ HCl(g)$
2. $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$
3. $S(s) + Cl_2(g) \rightarrow SCl_2(g)$
4. $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$
5. $2\ Li(s) + F_2(g) \rightarrow 2\ LiF(s)$
6. $H_2(g) + S(s) \rightarrow H_2S\ (g)$
7. $2\ Hg^{2+}(aq) + H_2(g) \rightarrow 2\ H^+(aq) + Hg_2^{2+}(aq)$

Jarape's lab



http://jarapesciencecartoons.blogspot.com/

The number of electrons gained in reduction always equals the number of electrons lost in oxidation. This is an important concept that you will use in balancing redox reactions.

The last part of section 4.04 deals with the classes of oxidation-reduction reactions. It's worth looking them over since knowing the categories will help you see the redox process more clearly. You will not have to memorize the details of the reactions within a category. Just know the general idea of what's happening in terms of redox.

1. Combustion Reactions… pretty obvious
2. Displacement Reactions… nicely named
    (a) Hydrogen displacement
    (b) Metal displacement
    (c) Halogen displacement
3. Disproportionation Reactions… fun to say and spell, more about these at the end of the summary

19.01 Balancing Redox Reactions

The method shown in Chang is a classic, complete description that will enable you to balance even the most complex oxidation-reduction reactions.

The AP Chem curriculum expects that you can use oxidation-reduction principles in balancing redox reactions, but the AP redox will not be as complex. This abbreviated set of instructions will get you to AP Chem level.

Step #1: **Find the elements that change oxidation numbers** by identifying the oxidation-reduction numbers of each atom in the reaction. The atoms that do not change the oxidation number can be ignored.

The **oxidized** element **increases its oxidation number**.
The **reduced** element **decreases its oxidation number**.

Step #2: **Write the two half reactions**, which indicate the gain or loss of electrons. There must be one substance oxidizing, and another reducing.

The oxidation half-reaction is shown with "lost" electrons as a product.

$X \rightarrow X^{+2} + 2\,e^-$

The reduction half-reaction is shown with "gained" electrons on the reactant side.

$Z^{+7} + 5\,e^- \rightarrow Z^{+2}$

NB: In each half-reaction, the **sum of the charges of the reactants = sum of the charges of the products**.

Step #3: **Use coefficients to balance the two half-reactions so that the oxidation-reduction electrons are equal.** The big idea in oxidation reduction is that the number of electrons lost in the oxidation half-reaction must equal the number of electrons gained in the reduction reaction.

Ox: $5 \times (X \rightarrow X^{+2} + 2\,e^-)$ $\quad 5\,X \rightarrow 5\,X^{+2} + \mathbf{10}\,\boldsymbol{e^-}$
Red: $2 \times (Z^{+7} + 5\,e^- \rightarrow Z^{+2})$ $\quad 2\,Z^{+7} + \mathbf{10}\,\boldsymbol{e^-} \rightarrow 2\,Z^{+2}$

Step #4: **Use those balanced Red-Ox half-reactions as the basis for balancing the main reaction.**

$5\,X + 2\,Z^{+7} \rightarrow 5\,X^{+2} + 2\,Z^{+2}$

Step #5: Check your reaction to be sure that the total charge of the reactants equals the products. (+14 on both sides of the reaction in this example.)

Step #5 is as far as you need to go for the AP Chemistry exam.

AP Chem exam questions no longer require that you perform Step #6.

Step #6: Balance the rest of the reaction based on the redox coefficients in acidic and alkaline conditions.

The last step often involves H^+ or OH^- and water molecules to balance "spectator" atoms that have not been oxidized or reduced.

EXAMPLE #1: $\ldots HNO_3(aq) + \ldots H_3AsO_3(aq) \rightarrow \ldots NO(g) + \ldots H_3AsO_4(aq) + \ldots H_2O(l)$

The redox half reactions:

$3\,e^- + N^{+5} \rightarrow N^{+2}$ Reduction
$As^{+3} \rightarrow As^{+5} + 2\,e^-$ Oxidation

Balance the two half reactions so that the electrons reduced equal the electrons oxidized.

$\mathbf{6}\,\boldsymbol{e}^- + 2\,N^{+5} \rightarrow 2\,N^{+2}$ Reduction (multiplied by 2 to get 6e$^-$ reduced)
$3\,As^{+3} \rightarrow 3As^{+5} + \mathbf{6}\,\boldsymbol{e}^-$ Oxidation (multiplied by 3 to get 6e$^-$ oxidized)

Therefore, in the balanced reaction, there must be 2 N for every 3 As

Therefore, these coefficients would be placed in the balanced reaction.

$\mathbf{2}\,HNO_3(aq) + \mathbf{3}\,H_3AsO_3(aq) \rightarrow \mathbf{2}\,NO(g) + \mathbf{3}\,H_3AsO_4(aq) + \ldots H_2O(l)$

... this is as far as AP Chem expects you to go.

Logically though, you could figure out the coefficient for the water… 1

EXAMPLE #2 $\ldots Cr_2O_7^{2-} + \ldots H^+ + \ldots H_2C_2O_4 \rightarrow \ldots Cr^{3+} + \ldots H_2O + \ldots CO_2$

Find the Red Ox:
$3\,e^- + Cr^{+6} \rightarrow Cr^{+3}$ Reduction
$C^{+3} \rightarrow C^{+4} + 1\,e^-$ Oxidation

Balance the two half reactions so that the electrons gained equal the electrons lost:

$\mathbf{3}\,\boldsymbol{e}^- + Cr^{+6} \rightarrow Cr^{3+}$ Reduction
$3\,C^{+3} \rightarrow 3\,C^{+4} + \mathbf{3}\,\boldsymbol{e}^-$ Oxidation

There must be 3 times as many atoms of C as Cr so that the electrons in reduction equal the electrons in oxidation.

Put the Red Ox coefficients on the reactants and products.

$\mathbf{1}\,Cr_2O_7^{2-} + H^+ + \mathbf{3}\,H_2C_2O_4 \rightarrow \mathbf{2}\,Cr^{3+} + \ldots H_2O + \mathbf{6}\,CO_2$

For the AP Chem exam this as far as you will have to go.

But for us compulsives who want to balance the entire equation, note that the reacting oxygen atoms are fixed at 19. Therefore, adjust the water so that the oxygen products have 19 oxygen atoms.

$\mathbf{1}\,Cr_2O_7^{2-} + H^+ + \mathbf{3}\,H_2C_2O_4 \rightarrow \mathbf{2}\,Cr^{3+} + \mathbf{7}\,H_2O + \mathbf{6}\,CO_2$

Finally, take care of the hydrogen ions and water (or you could balance the charges with the H$^+$)…..8

Example Problems:

1. $\ldots Cr^{3+} + H_2O + \ldots ClO_3^- \rightarrow \ldots Cr_2O_7^{2-} + \ldots ClO_2 + 2\,H^+$

2. $\ldots MnO_4^-(aq) + \ldots Cl^-(aq) + 16\,H^+(aq) \rightarrow \ldots Mn^{2+}(aq) + \ldots Cl_2(aq) + 8\,H_2O$

Answers on the last page and there are two videos that you will find at the AP16 Classroom page.

4.4 Disproportionation Reactions

Now that you have covered the typical oxidation-reduction reactions, this special reaction will be easier to understand.

Some compounds can undergo both oxidation and reduction in the same reaction. These can be recognized by finding two versions of the same element as a product, each with a different oxidation number. One version of the product has the reactant element oxidized and the other version of the product has the same reactant element reduced.

Understand these two important disproportionation reactions:

The action of diatomic chlorine gas in an alkaline solution. This reaction oxidizes the diatomic chlorine into the hypochlorous ion which is used as a disinfectant and bleach. The diatomic chlorine is also simultaneously reduced into the common chloride ion.

$$\overset{0}{Cl_2} + 2\,OH^- \rightarrow \overset{+1}{Cl}O^- + \overset{-1}{Cl^-} + H_2O$$

The two half-reactions each involve elemental chlorine:

Ox: $\frac{1}{2}\,Cl_2 \rightarrow Cl^{+1} + 1\,e^-$

Red: $\frac{1}{2}\,Cl_2 + 1\,e^- \rightarrow Cl^{-1}$

The decomposition of a peroxide to make oxygen is the second important disproportionation reaction. The peroxide oxygen is reduced to oxygen -2 in water and also oxidized to 0 as elemental oxygen.

$$2\,H_2\overset{-1}{O_2} \rightarrow 2\,H_2\overset{-2}{O} + \overset{0}{O_2}$$

The two half-reactions each involve peroxide.

Ox: $2\,O^{-1} \rightarrow O_2 + 2\,e^-$

Red: $2\,O^{-1} + 2\,e^- \rightarrow 2\,O^{-2}$

There will be another summary for the rest of the sections in the chapter.

Answers

1. SO_2 — S +4 O -2
2. CO_3^{2-} — C +4 O -2
3. K_2SO_4 — K +1 S +6 O -2
4. P_2O_5 — P +5 O -2
5. I_2 — I_2^0
6. NH_4^+ — N -3 H +1
7. $Na_2Cr_2O_7$ — Na +1 Cr +6 O -2
8. $Ca(OH)_2$ — Ca +2 O -2 H +1

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0 0 +1 -1

1. $H_2(g) + Cl_2(g) \rightarrow 2\ HCl(g)$

   H_2 oxidized (oxidation number increases from 0 to +1)

   Cl_2 reduced (oxidation number decreases from 0 to -1)

0 0 -3 +1

2. $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$

   H_2 oxidized

   N_2 reduced

0 0 +2 -1

3. $S(s) + Cl_2(g) \rightarrow SCl_2(g)$

   S oxidized

   Cl_2 reduced

0 0 +4 -2

4. $N_2(g) + 2\ O_2(g) \rightarrow 2NO_2(g)$

   $N_2(g)$ oxidized

   $O_2(g)$ reduced

0 0 +1 -1

5. $2Li(s) + F_2(g) \rightarrow 2\ LiF(s)$

   Li oxidized

   F_2 reduced

0 0 +1 -2

6. $H_2(g) + S(s) \rightarrow H_2S$

   H_2 oxidized

   S reduced

+2 0 +1 +1

7. $2\ Hg^{+2}(aq) + H_2(g) \rightarrow 2H^+(aq) + Hg_2^{+2}(aq)$

   H_2 oxidized

   Hg reduced

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1. $2\ Cr^{3+} + H_2O + 6\ ClO_3^- \rightarrow Cr_2O_7^{2-} + 6\ ClO_2 + 2\ H^+$ video on AP16 Classroom Unit 16 Page Example 1

2. $2\ MnO_4^- + 10\ Cl^- + 16\ H^+ \rightarrow 2\ Mn^{2+} + 5\ Cl_2 + 8\ H_2O$ video on AP16 Classroom Unit 16 Page Example 2