Oxidation / Reduction Handout

The original concept of "*oxidation*" applied to reactions where there was a "*union with oxygen*". The oxygen was either furnished by elemental oxygen or by compounds containing oxygen. Likewise then, "*reduction*" applied to reactions where there was a "*removal of oxygen*". (King, 74) These definitions though were given prior to the structure of atoms being fully understood.

The updated definition gives "*oxidation as the loss of electrons*". The loss of electrons occurs due to oxidizing agents. So, oxidizing agents are reactants that gain electrons. Likewise, "*reduction is the gain of electrons*". Reducing agents are responsible for reduction and they lose electrons. There is a mnemonic used to help remember the direction in which the electrons flow. The mnemonic is "LEO the lion says GER".

L *oss of*
E *lectrons is*
O *xidation*

G *ain of*
E *lectrons is*
R *eduction*

Another common mnemonic is OIL RIG for "*<u>O</u>xidation <u>I</u>s <u>L</u>oss*" of electrons and "*<u>R</u>eduction <u>I</u>s <u>G</u>ain*" of electrons.

Also keep in mind, the reducing agents are always oxidized; and, the oxidizing agents are always reduced. One process cannot occur without the other. If something is oxidized, then something else must be reduced at the same time.

*(**Remember:** Reducing agents are oxidized. Oxidizing agents are reduced.)*

<u>Oxidation Numbers</u>

In order to keep track of electron transfers in oxidation-reduction reactions, it is convenient to introduce the concept of oxidation numbers. The oxidation number of an atom is the charge which the atom *appears* to have when its valence electrons are counted according to some fairly arbitrary rules:

a.) electrons shared between like atoms are divided equally between the sharing atoms; and,

b.) electrons shared between two unlike atoms are counted with the more electronegative atom.

More specifically, the following rules may be used to determine the oxidation numbers for various types of atoms.

(***Note:** Oxidation number is NOT the same thing as valence. It is very important that you do NOT confuse the oxidation number with the ionic charge. While in some cases they are similar, for the most part they are not. Also, ionic charges are real properties of atoms; whereas, oxidation numbers are merely a theoretical construct that was created to make balancing equations easier. Thus, we do not need to understand the bonding within the chemicals in order to be able to use oxidation numbers effectively*.)

Rules for Determining Oxidation Numbers

1.) The total electric charge of a molecule is zero (0). All oxidation numbers must be consistent with the conservation of charge. So the charge must be conserved in the sense that the sum of all of the apparent charges must equal the net charges of the particle. That is, the sum of the positive charges must equal that of the negative charges.

2.) The electric charge of an element is zero (0). This applies to all elements regardless of how complicated they are. This rule applies to any pure substance whether it is a diatomic gas like oxygen O_2 or a piece of pure metal like iron. The examples given (iron, hydrogen, sodium, phosphorus, and sulfur) all have the oxidation number of zero.

Fe	H_2	Na	P_4	S_8
0	0	0	0	0

3.) The oxidation number of a monatomic ion is its ionic charge. In these cases the apparent charge of the atom is the real charge of the ion.

a. For Group I elements (the alkali metals), the oxidation number is +1 in all compounds.

Li^+	Na^+	K^+	Rb^+	Cs^+
+1	+1	+1	+1	+1

b. Likewise, for Group II elements (the alkaline earth metals), the oxidation number is always +2.

Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Ra^{2+}
+2	+2	+2	+2	+2

c. The Group VII elements – Fluorine always has an oxidation number of -1 in its compounds. The other halogens have oxidation number -1 in their compounds, except in compounds with oxygen and with other halogens, where they can have positive oxidation numbers. The halides always have an oxidation number of -1 in binary metallic compounds.

$NaCl$	$FeBr_2$	GaI_3
-1	-1	-1

4.) The oxidation number of H is +1 except when it is in a hydride of a metal and then it is -1. In the case of hydrides, the hydrogen is bonded to an atom that is less electronegative than the hydrogen. For example, in sodium hydride (NaH) the sodium is less electronegative than the hydrogen, so both electrons are counted with the hydrogen giving it a -1 charge.

H_2O	HNO_3	$Ca(OH)_2$	CaH_2
+1	+1	+1	-1

5.) The oxidation number of oxygen, O, is -2, except in peroxides where it is -1 and superoxides where it is – ½ and in instances where it is bound to fluorine.

H_2O	$KClO_3$	PbO_2
-2	-2	-2

a. In peroxides, there is a bond between like atoms, so the electrons are shared between them. For example, in hydrogen peroxide (H-O-O-H), the electrons in the hydrogen-oxygen bond are counted with the more electronegative oxygen. For the oxygen-oxygen bond, the electron pair is shared between the two oxygen atoms. This results in an apparent charge on the oxygen of -1.

H_2O_2	BaO_2
-1	-1

b. In sodium and potassium superoxides, there is a double bond between each of the oxygens and the central metal atom. This results in the apparent charge of – ½ for each oxygen to balance out the +1 charge on the metal.

$O{=}K^{+}{=}O$	$O{=}Na^{+}{=}O$
-½ -½	-½ -½

(***Note:*** *Fractional oxidation numbers are not common; however, they are allowed in order to maintain a consistent set of rules*.)

c. Another exception which is less common is when **oxygen is bound to fluorine**, the only atom which is more electronegative than oxygen. In an oxygen-fluorine bond, the shared electrons are counted with the more electronegative fluorine. For example, oxygen difluoride (OF_2) yields an oxidation number of -1 for each of the fluorines and +2 for oxygen.

OF_2
+2 -1

6.) For complex ions or polyatomic ions (*charged particles with more than one kind of atom*), the oxidation numbers of all of the atoms must add up to the charge on the ion. The charge of the polyatomic ion is a property of the entire ion, while the oxidation numbers are assigned to each individual atom. For example, the sulfate ion, SO_4^{2-}, has an overall charge of -2, so the oxidation numbers must add up to -2.

7.) The oxidation number of nonmetals in oxygen acids and similar compounds is the charge needed to make the molecule electrically neutral once the oxidation numbers for H, O, and the metal atoms have been assigned.

Balancing Half-Reactions

The change in the oxidation number of an atom shows the number of electrons it has gained or lost. We can use this number of electrons to balance half-reactions. When the half-reaction is balanced the sum of the ionic charges on the left side of the equal sign is equal to that on the right side.

It is not necessary to determine the oxidation numbers prior to figuring out the number of electrons involved in a half-reaction. One may simply balance the half reaction equations by adding the appropriate number of electrons. The complete reaction equation then is obtained by adding the two half-reactions together. To do this though, we need to first verify that the same number of electrons are involved in both the oxidation and the reduction portions. (Pierce 137)

The rules for balancing redox reactions are relatively simple and need to be followed in order. Any steps that are not relevant may be skipped, but the order of the steps should be maintained.

Rules for Balancing Half-Cell Reactions

(*Another mnemonic: "**Rule of Thumb**" – Prior to balancing any reaction, place your thumb over elemental hydrogen. This is to remind you to balance the hydrogen last. If there is no hydrogen, place your thumb over the elemental oxygen*.)

1.) Identify the reactants on the left side of the equation (arrow) and the products on the right of an unbalanced equation.

2.) Assign each atom in each molecule the appropriate oxidation number. Identify the elements which show the change of valence and indicate the valence of each atom above its symbol.

3.) Break the equation into halves to create two equations.
   a. The reactants in each half equation need to go to their exact products.
   b. At this point, do NOT worry about how many of each atom type there is in the products at this stage

Then for each half-cell:

4.) Balance the numbers of atoms on both sides. Determine the gain and loss and what coefficients are required to make the gain and loss equal

5.) Balance any oxygen atoms by adding water molecules to the OPPOSITE side of the equation (arrow).

6.) Balance the number of water molecules, by adding H^+ ion (acidic solution) or OH^- (basic solution) to the left or right side of each half-cell as required.

7.) Add electrons (each one represents a -1 charge) to the appropriate side of the equation to make the charges on each side equal.

8.) Take both half equations and multiply one or both by the appropriate number such that they both have the same number of free electrons in each half-cell.

9.) Add both half reactions together again.

For the full equation:

10.) Cancel out any parts that are identical on both sides of the equation. The electrons will always be eliminated because we guaranteed that they were equal prior to adding the half-cells together. Also, the H+ and water molecules are generally either partially or completely eliminated.

Sample Problem:

Given the following unbalanced reaction:

$$Zn_{(s)} + VO^{2+}{}_{(aq)} \rightarrow Zn^{2+}{}_{(aq)} + V^{3+}{}_{(aq)}$$

Step 1: Assign the oxidation numbers to all atoms on both sides of the equation to determine which are oxidized and which are reduced.

$$\underset{0}{Zn} + \underset{+4\ \ -2}{VO^{2+}} \rightarrow \underset{+2}{Zn^{2+}} + \underset{+3}{V^{3+}}$$

Step 2: Write 2 unbalanced half-cell equations, one for the species that is oxidized and its product; and, one for the species that is reduced and its product.

oxidation: $Zn \rightarrow Zn^{2+}$

reduction: $VO^{2+} \rightarrow V^{3+}$

Step 3: Insert coefficients to make the numbers of atoms of all elements (except oxygen and hydrogen) equal on the two sides of the equation.

This is not necessary here because zinc and vanadium are already balanced in the 2 half-cell reactions. No other atoms appear, except for oxygen. So step 3 is complete.

Step 4: Balance oxygen by adding H_2O to the left or right side of each half-cell reaction.

This step is not necessary for the oxidation portion: $Zn \rightarrow Zn^{2+}$

reduction: $VO^{2+} \rightarrow V^{3+} + H_2O$

Step 5: Balance the hydrogen by adding H^+ ion (acidic solution) or OH^- (basic solution) to the left or right side of each half-cell as required.

reduction: $VO^{2+} + 2\ H^+ \rightarrow V^{3+} + H_2O$

Step 6: Balance the charge by inserting electrons, e^-, as a reactant in the reduction half-cell and as a product in the oxidation half-cell.

oxidation: $Zn \rightarrow Zn^{2+} + 2\ e^-$

reduction: $VO^{2+} + 2\ H^+ + e^- \rightarrow V^{3+} + H_2O$

Step 7: Multiply the 2 half-cell equations by numbers chosen to make the number of electrons given off by the oxidation equal the number of electrons take up by the reduction.

oxidation (x 1): $Zn \rightarrow Zn^{2+} + 2\ e^-$

reduction (x 2): $2\ VO^{2+} + 4\ H^+ + 2\ e^- \rightarrow 2\ V^{3+} + 2\ H_2O$

Step 8: Add the 2 half-cell equations to cancel electrons. If H^+ ion, OH^- ion, or H_2O appear on both sides of the final equation, cancel out the number that are duplicated.

$$Zn \rightarrow Zn^{2+} + 2\ e^-$$

$$\underline{2\ VO^{2+} + 4\ H^+ + 2\ e^- \rightarrow 2\ V^{3+} + 2\ H_2O}$$

$$Zn + 2\ VO^{2+} + 4\ H^+ \rightarrow Zn^{2+} + 2\ V^{3+} + 2\ H_2O \qquad \text{(Final Answer.)}$$

(*Note:* Free electrons should never appear in the final answer.)

Step 9: If you are asked to solve the equation in a **basic solution**, complete steps 1-8 and then add H_2O to the “final answer” to cancel out the protons.

$$Zn + 2\ VO^{2+} + 4\ H^{+} \rightarrow Zn^{2+} + 2\ V^{3+} + 2\ H_2O \qquad \text{(From Step 8.)}$$

$$\underline{\qquad 2H_2O \rightarrow 4\ H^{+} + 4\ OH^{-} \qquad -}$$

$$Zn + 2\ VO^{2+} + 2\ H_2O \rightarrow Zn^{2+} + 2\ V^{3+} + 4\ H^{+} + 4\ OH^{-} \qquad \text{(Basic)}$$

(*Note:* Free electrons still do not appear in the final answer.)

References

Binford, Jr., Jesse S. Foundations of Chemistry. Macmillan Publishing Co., Inc.: 1977. (pp. 261-288)

Hopkins, B. Smith and John C. Bailar, Jr. General Chemistry for College, 4th ed.. D. C. Heath & Co. Boston: 1951. (pp. 194-200)

King, W. Bernard. Elementary Chemistry for College Students, rev. ed. Littlefield, Adams & Co. Paterson, NJ: 1960. (pp. 74-83)

Lewis, John R. College Chemistry, 9th ed. Barnes & Noble, Inc. New York: 1971. (pp. 139-144)

Oxtoby, David W., Norman H Nachtrieb, and Wade A. Freeman. Chemistry: Science of Change. Chicago: 1990. (pp. 137-140; 490-500)

Pierce, Conway and R. Nelson Smith. General Chemistry Workbook: How to Solve Chemistry Problems, 3rd ed. W. H. Freeman and Co. San Francisco: 1965. (pp. 131-140)

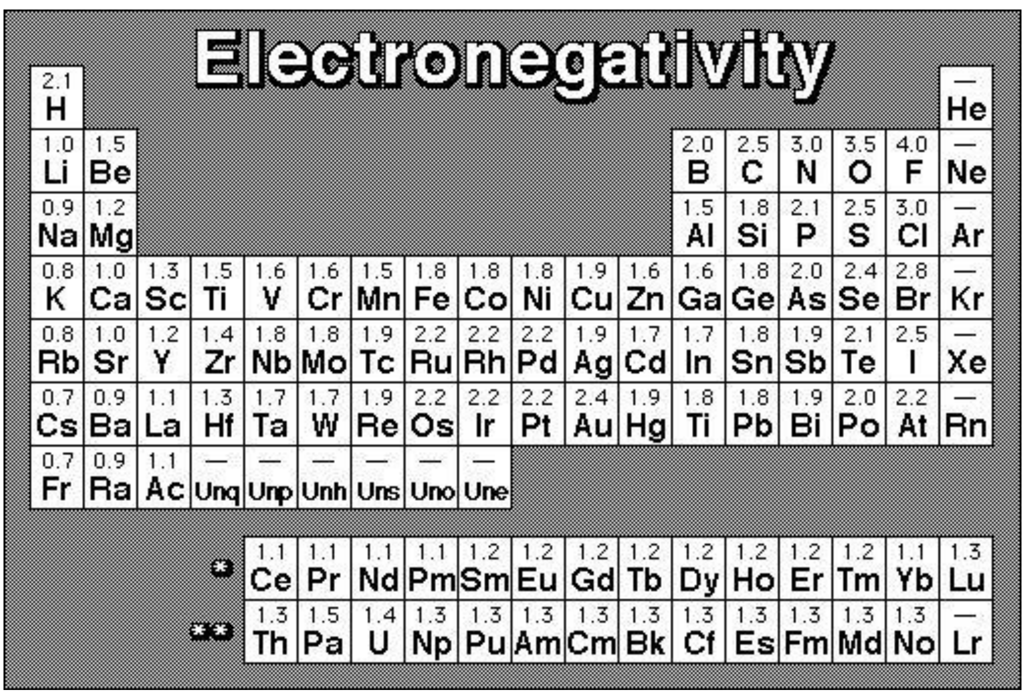
Sienko, Michell J. and Robert A. Plane. Chemistry: Principles and Properties. McGraw-Hill. New York: 1966. (pp. 84-90)

Tro, Nivaldo J. Chemistry: A Molecular Approach, 2nd ed. Prentice Hall. Indianapolis: 2011. (pp. 162-169)

http://www.green-planet-solar-energy.com/oxidation-number-rules.html

http://www.green-planet-solar-energy.com/balancing-redox-reactions.html

Chart of electronegativity



Name: ______________________________

Sec #: ____________ **Date:** ________________

Oxidation / Reduction Worksheet

1. Define the following terms:

a.) Oxidation –

b.) Reduction –

c.) Oxidation number –

d.) Oxidizing Agent –

e.) Reducing Agent –

2. Assign oxidation numbers to the following atoms in each compound:

(Ones with "" are exceptions to the oxygen rule. Check page 3.)*

a. $NaCl$

b. $Fe_2(SO_4)_3$

c. I_2

d. $KMnO_4$

e. CaH_2

f. $SnCl_4$

g.* BaO_2

h. CO_2

i.* H_2O_2

3. Identify the <u>oxidizing agent</u> and <u>the reducing agent</u> in each of the following reactions.

Write the answers in the corresponding blanks to the left of the reactions.
(Note: For one of these, the same species is both the oxidizing <u>and</u> the reducing agent.)

<u>Oxidizing</u> **<u>Reducing</u>**

______ ______ a.) $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

______ ______ b.) $Cr_2O_7^{2-} + 6\ I^- + 14\ H^+ \rightarrow 2\ Cr^{3+} + 3\ I_2 + 6\ H_2O$

______ ______ c.) $Cl_2 + H_2O \rightarrow HCl + HOCl$

4. Multiple Choice – Write the correct answer in the blank to the left of the questions.

_____ a.) Which metal is in the **<u>lowest oxidation state (i.e., has the lowest oxidation number)</u>**?

A. $CrCl_3$ B. Cu C. $FeCO_3$ D. MnO_2

_____ b.) In which species does sulfur leave the **<u>same oxidation number</u>** as the chlorine in $\mathbf{ClO_2^-}$?

A. H_2S C. SO_3^{2-}

B. S_8 D. none of the above

_____ c.) The oxidation number of sulfur in $\mathbf{SO_3^{2-}}$ is the **<u>same as the oxidation number</u>** of carbon in?

A. CO B. $K_2C_2O_4$ C. $C_2H_3O_2^-$ D. CO_2

_____ d.) The **<u>oxidation state of iodine</u>** in the equation below changes from ____ to _____.

$$\mathbf{2\ IO_3^-{}_{(aq)} + 5\ HSO_3^-{}_{(aq)} \rightarrow I_{2\ (s)} + 5\ SO_4^{2-}{}_{(aq)} + H_2O\ (l) + H^+{}_{(aq)}}$$

A. +7 to -1 B. +5 to +1 C. +5 to 0 D. +3 to 0

5. Using the <u>half-cell reaction method</u>, balance the following redox reactions:

$$Fe^{2+}{}_{(aq)} + MnO_4^-{}_{(aq)} + H^+{}_{(aq)} \rightarrow Fe^{3+}{}_{(aq)} + Mn^{2+}{}_{(aq)} + H_2O_{(l)}$$

<u>a.) First, Assign Oxidation Numbers to the atoms in the equation above</u>.

<u>b.) Then, Use Half-Cell Method to solve</u>:

Bonus Page – Balancing A Basic Oxidation – Reduction Reaction

This page is optional.

6. Using the <u>half-cell reaction method</u>, balance the following redox reactions:

$$Ag_{(s)} + HS^{-}_{(aq)} + CrO_4{}^{2-}_{(aq)} \rightarrow Ag_2S_{(s)} + Cr(OH)_{3\,(s)}$$

<u>a.) First, Assign Oxidation Numbers to the atoms in the equation above</u>.

<u>b.) Then, Use Half-Cell Method to solve:</u>

(*Since this one is basic, solve as usual, but then add H_2O to cancel out the protons.*)