CHE 112 Electrochemistry

Oxidation – Reduction (REDOX) Reactions

A. Introduction

Historically, oxidation meant reacting with oxygen. Nowadays, oxidation is a much more general term.
Oxidation means a substance has ‘lost electrons’.
Reduction means a substance has ‘gained electrons’.
Oxidation & reduction occur together, such that electrons are actually **transferred** from one substance to another.
A useful mnemonic is ‘LEO GER’ – Loss of Electrons is Oxidation, Gain of Electrons is Reduction.

Example of a REDOX rxn: $2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$

Oxidation Half Rxn	$2Na \rightarrow 2Na^+ + 2e^-$
Reduction Half Rxn	$Cl_2 + 2e^- \rightarrow 2Cl^-$
Overall Rxn	$2Na(s) + Cl_2(g) \rightarrow 2Na^+ + 2Cl^-$

Notice when the two half reactions are added, the $2e^-$’s subtract out, showing they are simply transferred from Na to Cl_2. Na lost electrons, so it is oxidized. Cl_2 gained electrons, so it is reduced.

B. Oxidation Numbers – are a bookkeeping device which make analyzing more complicated REDOX rxns simpler.

Oxidation Numbers are the charge an atom would have if the bonding electrons were assigned to the more electronegative element. (Recall, electronegativity is the tendency of a bonded atom to attract the bonding electrons. There is a chart of electronegativity values for elements in the textbook.)

If an element’s oxidation number increases during the reaction, it is oxidized.
If an element’s oxidation number decreases (reduces) during the reaction, it is reduced
(Be sure to consider algebraic sign…)

Examples of determining oxidation numbers of atoms in a molecule:

a. H_2O Draw the Lewis Dot Structure for H_2O. In the structure O has two bonding pairs & two nonbonding pairs of electrons about it. O is more electronegative than H, so all the electrons are assigned to O (just on paper, not for real). Then, we can fill in this chart:

	O	H
# valence e^-'s, neutral atom	6	1
# valence e^-'s after assignment	8	0
'pseudo charge' = oxidation #	-2	+1

b. Cl_2 Draw the Lewis Dot Structure for Cl_2. In the structure each Cl has 8 surrounding electrons. Both Cl's are as electronegative as the other, so the bonding electrons must be evenly divided. Now each Cl has 7 surrounding electrons. Then, we can fill in this chart:

	Cl	Cl
# valence e^-'s, neutral atom	7	7
# valence e^-'s after assignment	7	7
'pseudo charge' = oxidation #	0	0

In fact, the oxidation number always = 0 for an element in its **elementary** form.

Rather than having to draw Lewis Dot Structures all the time, there are some shortcut Rules for Determining Oxidation Numbers:

1. Oxid # = 0 for an element in its elementary form.

2. Oxid # = charge for a monatomic ion.

3. Σ Oxid #'s = net charge for a polyatomic species.

4. Certain elements have the same oxidation # in all or almost all of their **compounds**:

Element occurring in a cmpd	Oxidation #
Alkali Metals	+1
Alkaline Earth Metals	+2
B & Al	+3
F	-1 (all cmpds)
H	+1 (most cmpds)
H	-1 (metal hydrides)
O	-2 (most cmpds)
O	-1 (peroxides)

Examples of Determining Oxidation Numbers using the rules:

a) Find the oxidation # of all atoms in Na_2CrO_4.

Note that the net charge on this polyatomic species is zero since it is a compound. Using the rules, Na's oxid # is +1 & O's oxid # is -2. Let x = Cr's oxid #, & then determine it using rule 3:

$2(+1) + x + 4(-2) = 0$

So x = +6 for Cr

b) Find the oxidation number of all atoms in NO_3^-.
Note that the net charge on this polyatomic species is -1. Using the rules, O's oxid # is -2. Let x represent N's oxid #, & then determine it using rule 3:

$x + 3(-2) = -1$

so x = +5 for N

Using Oxidation Numbers to analyze REDOX reactions:

$$HCl(g) + HNO_3(l) \rightarrow NO_2(g) + \tfrac{1}{2}Cl_2(g) + H_2O(l)$$

Above each atom in the equation, jot down its oxidation #. (Be sure you write the oxidation number per atom – i.e., each O in HNO_3 is -2. Do not multiply by 3!)
Then apply the rule: If oxid # increases, species is oxidized. If Oxid # decreases, species is reduced. This is what you should find:

	H	Cl	N	O
Reactant side	+1	-1	+5	-2
Product side	+1	0	+4	-2
		increase	decrease	

Therefore, we say HCl is oxidized & HNO_3 is reduced.

Important terminology:

HNO_3 is the **oxidizing agent** of HCl. HNO_3 is reduced while acting as the oxidizing agent.

HCl is the **reducing agent** of HNO_3. HCl is oxidized while acting as the reducing agent.

C. Balancing REDOX reactions by the Half Reaction Method:

1. Split into half reactions by analyzing oxidation numbers.
2. For each half rxn, do mass balance (i.e., balance so as to have the same number of each type of atom on both sides.)
   - Introduce H_2O to balance O
   - Introduce H^+ to balance H
3. For each half rxn, do charge balance.
4. Multiply each half rxn so as to make the number of electrons lost = the number of electrons gained.
5. Add the half reactions and simplify.
6. If balancing for basic (alkaline) conditions: Notice the number of H^+ in the reaction. Then add that same number of OH^- to both sides. Simplify by noting that $H^+ + OH^-$ gives H_2O.

Example: Balance $ClO_3^-(aq) + H_2S(g) \rightarrow Cl^-(aq) + SO_4^{2-}(aq)$

1. Notice that S's oxidation numbers increase from -2 to +6 (reactant side to product side), so it is oxidized.

Cl's oxidation numbers decreases from +5 to -1, so it is reduced.

OXID $H_2S \rightarrow SO_4^{2-}$

REDN $ClO_3^- \rightarrow Cl^-$

2. Now do mass balance for each half reaction:

$H_2S + 4H_2O \rightarrow SO_4^{2-} + 10\,H^+$

$ClO_3^- + 6H^+ \rightarrow Cl^- + 3H_2O$

3. Now do charge balance for each half reaction:

$H_2S + 4H_2O \rightarrow SO_4^{2-} + 10\,H^+ + 8e^-$ (oxidation, e's must be on product side)

$ClO_3^- + 6H^+ + 6e^- \rightarrow Cl^- + 3H_2O$ (reduction, e's must be on reactant side)

4. Now multiply appropriately to make #e's lost = #e's gained.

$3 \times (H_2S + 4H_2O \rightarrow SO_4^{2-} + 10\,H^+ + 8e^-)$

$4 \times (ClO_3^- + 6H^+ + 6e^- \rightarrow Cl^- + 3H_2O)$

5. Add and simplify.

$3H_2S(g) + 4ClO_3^-(aq) \rightarrow 3SO_4^{2-}(aq) + 4Cl^-(aq) + 6H^+(aq)$

This is balanced for acidic conditions.

6. If balancing for basic conditions, add 6 OH^- to both sides & simplify to:

$3H_2S(g) + 4ClO_3^-(aq) + 6\ OH^-(aq) \rightarrow 3SO_4^{2-}(aq) + 4Cl^-(aq) + 6H_2O(l)$