Name ____________________________ **Chem 163 Section**: ______ **Team Number:** ______

ALE 23. Balancing Redox Reactions

(Reference: Section 4.5 (pp. 158 – 166) and 21.1 Silb*erberg 5th edition*)

How does one balance a reaction for both matter and charge?

The Model

Oxidation-reduction or **Redox reactions** involve the transfer of one or more electrons from one chemical species to another. Redox reactions are involved in the corrosion of metals, the combustion of fuels, the generation of electricity from batteries and many biological processes including cellular respiration and photosynthesis. An understanding of redox chemistry is essential in the design of new kinds of batteries, increasing efficiency in fuel combustion, the prevention of corrosion, etc.

Recall from Chem 161 (Sec. 4.5 in *Silberberg*), the **oxidation number** of an atom is the "apparent" charge the atom would have if each of its bonding electrons were assigned to the more electronegative atom in each bond. Oxidation numbers are useful in determining the substance **oxidized** (**L.E.O.** = **L**oss of **E**lectron(s) is **O**xidation) and the substance **reduced** (**G.E.R.** = **G**ain of **E**lectron(s) is **R**eduction). Hence, the substance that is oxidized loses electrons and therefore serves as a **reducing agent** since it provides electrons to another atom thereby causing that atom to be reduced. The species being reduced serves as the **oxidizing agent** because it removes electrons from another substance, thereby causing that substance to be oxidized.

Rules to Assign Oxidation Numbers

Oxidation numbers are often written above the atomic symbol: $\overset{+1}{H}\overset{+5}{N}\overset{-2}{O}_3$ $\overset{0}{F}_2$ $\overset{-4}{C}\overset{+1}{H}_4$ $\overset{+1}{H}_2\overset{-1}{O}_2$

1) In **free elements** (*i.e.*, in the uncombined state), each atom has an oxidation number of zero.
   e.g. Al, S_8, Na, Fe, H_2, O_2, N_2, Cl_2 each have an O.N. = 0

2) Since **fluorine** is the most electronegative element, the oxidation number of fluorine in *all* of its *compounds* is -1.

3) The oxidation number of **oxygen** in most compounds (called "oxides") is -2. In **peroxides** (e.g. H_2O_2), the oxidation number of oxygen is -1. In **superoxides** (e.g. O_2^{1-}), the oxidation number of oxygen is -½.

4) The oxidation number of **hydrogen** is +1, except when it is bonded to metals in binary compounds (e.g. metallic hydrides: LiH, MgH_2), in which its oxidation number is -1.

5) Group **IA and IIA metals** form compounds in which the metal atoms have oxidation numbers of +1 and +2, respectively.

6) The sum of the oxidation numbers of all the atoms in a species must be equal to the net charge of the species. e.g. The sum of the O.N.'s of a molecular substance is zero: $\overset{+1}{H}_2\overset{-2}{O}$ $\overset{-4}{C}\overset{+1}{H}_4$ $\overset{+5}{Cl}\overset{-1}{F}_5$ $\overset{+4}{N}\overset{-2}{O}_2$
   The sum of the O.N.'s of the atoms in a polyatomic equals the charge of the ion:
   $(\overset{-2}{O}\overset{+1}{H})^-$ $(\overset{+6}{S}\overset{-2}{O}_4)^{2-}$ $(\overset{+3}{N}\overset{-2}{O}_2)^-$

Key Questions

1. The substances oxidized and reduced may not be obvious in the following redox reaction:

$$8\ H^{+}_{(aq)} + Cr_2O_7^{2-}{}_{(aq)} + 3\ SO_3^{2-}{}_{(aq)} \rightarrow 2\ Cr^{3+}{}_{(aq)} + 3\ SO_4^{2-}{}_{(aq)} + 4\ H_2O_{(l)}$$

   a. Write the oxidation numbers above each atomic symbol on the left and right sides of the reaction above.

   b. Does the oxidation number of any atom <u>*increase*</u>? Is that species the <u>*oxidizing agent*</u> or the <u>*reducing agent*</u>?

   c. Does the oxidation number of any atom <u>*decrease*</u>? Is that species the <u>*oxidizing agent*</u> or the <u>*reducing agent*</u>?

   d. Which species is being oxidized? ____________________

   e. Which species is being reduced? ____________________

Exercises

2. Write the oxidation number above each symbol in the following compounds or ions.

   a. KBr　　b. BrF_3　　c. $HBrO_3$　　d. CBr_4

   e. MnO_4^{1-}　　f. Mn_2O_3　　g. $KMnO_4$

3. Assign oxidation numbers to each atom in the following reaction and then identify the oxidizing agent, reducing agent, the substance oxidized and the substance reduced.

$$NO_3^{1-}{}_{(aq)} + 4\ Zn_{(s)} + 7\ OH^{1-}{}_{(aq)} + 6\ H_2O_{(l)} \rightarrow 4\ Zn(OH)_4^{2-}{}_{(aq)} + NH_{3\,(aq)}$$

   Oxidizing agent: ________________　　Reducing agent: ________________

   Substance oxidized: _____________　　Substance reduced: ______________

The Model: Balancing a Redox Reaction in an Acidic Solution

Example 1. Copper(I) chloride and arsenic precipitate out of solution when copper metal is added to tetraarsenic hexoxide in an acidic solution of chloride.

A. Write unbalanced reaction: $Cu + As_4O_6 + Cl^- \rightarrow CuCl + As$ (<u>Acidic condition</u>: when balanced, H^+ will be reactant or a product.)

B. Assign oxidation numbers and determine what's oxidized and reduced:

$$\overset{0}{Cu} + \overset{3+}{As_4}O_6 + Cl^- \rightarrow \overset{1+}{Cu}Cl + \overset{0}{As}$$

oxidation

reduction

Reducing agent: Cu. **Oxidizing agent: As_4O_6**

C. Determine the half-reactions:
Oxidation: $Cu + Cl^- \rightarrow CuCl$
Reduction: $As_4O_6 \rightarrow As$

D. Balance all elements except O & H: Reduction: $As_4O_6 \rightarrow 4\ As$

E. Use H_2O to balance oxygen atoms: Reduction: $As_4O_6 \rightarrow 4\ As + 6\ H_2O$

F. Use H^+ to balance hydrogen atoms: Reduction: $12\ H^+ + As_4O_6 \rightarrow 4\ As + 6\ H_2O$

G. Use e- to balance charge:
Oxidation: $Cu + Cl^- \rightarrow CuCl + e^-$
Reduction: $12\ e^- + 12\ H^+ + As_4O_6 \rightarrow 4\ As + 6\ H_2O$

H. Conserve # of e^- (# e^- lost = # e^- gained)
oxidation = $12\ Cu + 12\ Cl^- \rightarrow 12\ CuCl + 12\ e^-$
reduction = $12\ e^- + 12\ H^+ + As_4O_6 \rightarrow 4\ As + 6\ H_2O$

I. Combine the ½-reactions:

$$12\ Cu + As_4O_6 + 12\ Cl^- + 12\ H^+ + 12\ e^- \rightarrow 12\ CuCl + 4\ As + 6\ H_2O + 12\ e^-$$

J. Simplify algebraically to get the simplest whole number ratio and check to see if balanced by both charge and mass.

$$\mathbf{12\ Cu + As_4O_6 + 12\ Cl^- + 12\ H^+ \rightarrow 12\ CuCl + 4\ As + 6\ H_2O}$$

Key Questions

4. a. In step A of the model why was the product written as CuCl and not $Cu^+ + Cl^-$?

   b. According to the Model, how is the number of oxygen atoms balanced in each half-reaction?

   c. How is the number of hydrogen atoms balanced in each half-reaction?

   d. How is charge balanced in each half-reaction?

5 a. Why are the stoichiometric coefficients of the oxidation half reaction multiplied by 12 in Step H of example 1?

b. True or False: An oxidation reaction *must* occur at the same time that a reduction reaction takes place. *Justify your response*.

Exercise

6. The permanganate ion, MnO_4^-, reacts with oxalate, $C_2O_4^{2-}$, to yield manganese (IV) oxide and carbonate, CO_3^{2-}. Use the half-reaction method to balance this reaction in *acidic conditions*. *Show your work*.

The Model: Balancing a Redox Reaction in an Basic Solution

The reaction you balanced in exercise #6, above, between the permanganate ion and the oxalate ion occurs in basic solution—not in acidic solution! To balance a redox reaction in basic solution follow the steps used to balance an equation in acidic conditions (i.e. steps A – J on page 3) and then follow steps K – L, below.

Example 2. In a basic solution, permanganate reacts with oxalate to yield manganese(IV) oxide and carbonate.

This is what you should have ended up with in exercise #6, above, after completing steps A – J on page 3:

$$2\ MnO_4^- + 3\ C_2O_4^{2-} + 2\ H_2O \rightarrow 2\ MnO_2 + 6\ CO_3^{2-} + 4\ H^+$$

To balance this equation in basic solution …

K. Make the solution basic by adding OH- to each side:

$$2\ MnO_4^- + 3\ C_2O_4^{2-} + 2\ H_2O + 4\ OH^- \rightarrow 2\ MnO_2 + 6\ CO_3^{2-} + 4\ H^+ + 4\ OH^-$$

L. Neutralize the H+ and OH- to create water:

$$2\ MnO_4^- + 3\ C_2O_4^{2-} + 2\ H_2O + 4\ OH^- \rightarrow 2\ MnO_2 + 6\ CO_3^{2-} + 4\ H_2O$$

M. simplify algebraically, canceling any terms (e.g. water) that appear on both sides:

$$\mathbf{2\ MnO_4^- + 3\ C_2O_4^{2-} + 4\ OH^- \rightarrow 2\ MnO_2 + 6\ CO_3^{2-} + 2\ H_2O}$$

Key Question

7. Why in Step K of Example 2 is "4 OH^-" added to each side of the reaction? (Such a step did not take place in Example 1. What's different about Example 2?)

Exercises

Balance the following redox reactions by using the half-reaction method. *Show your work*.

8. Many metals dissolve in hydrochloric acids. Copper does not. To dissolve copper, one must use an oxidizing acid, such as nitric acid. Gold, however, does not dissolve even in nitric acid. To dissolve the unreactive metal, one must place gold in *aqua regia*, which is a mixture of concentrated nitric acid and concentrated hydrochloric acid. The unbalanced chemical equation for that process is:

$$Au + NO_3^- + Cl^- \rightarrow AuCl_4^- + NO \qquad \text{(acidic)}$$

9. Zinc is a reactive metal that dissolves readily in hydrochloric or in nitric acid. But zinc also dissolves in basic solutions containing the nitrate ion. The unbalanced chemical equation for that process is:

$$Zn + NO_3^- \rightarrow Zn(OH)_4^{2-} + NH_3 \qquad \text{(basic)}$$

10. A convenient way to volumetrically analyze solutions of sulfite (colorless) is to titrate them with an acidified standardized dichromate solution (orange).

$$SO_3^{2-} + Cr_2O_7^{2-} \rightarrow Cr^{3+} + SO_4^{2-} \qquad \text{(acidic)}$$

The resulting chromium (III) sulfate solution is green. Suppose 25.00 mL of a sodium sulfite solution is transferred to an Erlenmeyer flask and acidified. It is then titrated with 0.0628 *M* $K_2Cr_2O_7(aq)$. When 22.38 mL of the dichromate solution has been added, the first presence of orange indicates "left over" dichromate and the endpoint has been reached. What is the molarity of the original $Na_2SO_3(aq)$ solution? *Show your work*.