BALANCING REDOX EQUATIONS VIA HALF-REACTIONS

Preliminary Steps

Prior to beginning the mechanical process of balancing a redox equation, certain facts must be ascertained.

- **First**, one must determine precisely what the reactants and products are for the given reaction. That is one must know HOW that substance physically exists in the system. For example, HNO_3 exists in aqueous solution as H_3O^+ and NO_3^- ions and not as HNO_3. Likewise, $MgCl_2$ exists in solution as $Mg(H_2O)_6^{+2}$ and Cl^- ions and not Mg^{+2} and Cl^- ions.

- **Next**, One must recognize that not all of the solids, liquids, gases, and ions in a given reaction mixture are actually involved in the redox reaction. Therefore, one must determine which species ARE involved in the reaction. This is done by determining the oxidation states of all of the atoms in ALL of the reactants and products in the system and concluding which atoms are changing oxidation states.

- **Finally**, one picks out a product (which contains one of the atoms that changes oxidation state) and matches it with the reactant from which it is derived. This is repeated for the other product which involved atoms which underwent changes in oxidation state during the reaction. These two reactant/product pairs constitute the basis of the two HALF REACTIONS which will eventually be combined to give the properly balanced redox equation. Now that the reactants and products have been paired-up one can begin the mechanical process of balancing each half reaction.

Balancing Half-Reactions

The balancing of half-reactions is a simple four step process.

STEP 1. **Balance the half-reaction with respect to redox atoms.**
That is, pick a reactant/product pair and place the reactant on the left and the product on the right separated by an arrow. Put coefficients in front of these species so as to balance the number of the atoms that are changing oxidation states (the redox atoms).

STEP 2. **Balance the half-reaction with respect to oxidation states using electrons.**
That is, add electrons to one side so that the sum of the oxidation states of the redox atoms are equal.

STEP 3. **Balance the half-reaction with respect to charge using H_3O^+ in acidic solutions or OH^- in basic or neutral solutions.**
That is, add H_3O^+ ions (if in acidic solution) or OH^- ions (if in neutral or basic solution) to one side of the equation so that the sum of the charges (including electrons!) on the two sides are equal.

STEP 4. **Balance the half-reaction with respect to hydrogen and oxygen atoms using water.**
That is, add H_2O's to one side so as to balance the number of hydrogen and oxygen atoms on the two sides.

Combining half-reactions

The net redox equation is produced by combining two half-reactions. However, as electrons are never actually liberated in any chemical reaction, the two half reactions must be combined in such a manner so that the same number of electrons produced in the oxidation half-reaction are consumed in the reduction half-reaction. This is accomplished by multiplying each half reaction by a different coefficient so that the number of electrons produced equal the number of electrons consumed.

EXAMPLES

Example 1: Cu metal dissolves in 6M HNO_3 to produce blue $Cu(H_2O)_6^{+2}$ and NO gas. (NO_2 gas is also produced, but, colorless NO gas is the chief product below 6M, while NO_2 is the chief product at or above 6M, as in concentrated HNO_3, for example.)

Step 1:

$$NO_3^- \longrightarrow NO$$

Here, the N atom is changing oxidation so we need the same number of N atoms on the two sides.

Step 2:

$$3\ e^- + NO_3^- \longrightarrow NO$$

On the left side of the equation, the N atom in NO_3^- has a +5 oxidation state while in NO the N atom has only a +2 oxidation state. Therefore, 3 e^-'s are needed on the left side to balance the oxidation states.

I.e., $+5 + 3x(-1) = +2$

Step 3:

$$4\ H_3O^+ + 3\ e^- + NO_3^- \longrightarrow NO$$

By adding 4 H_3O^+ ions the total charge on the left and right sides of the equation are equal.

I.e., $+4 + 3x(-1) + (-1) = 0$

Step 4:

$$4\ H_3O^+ + 3\ e^- + NO_3^- \longrightarrow NO + 6\ H_2O$$

Finally, by adding 6 H_2O's to the right side the number of hydrogen atoms (and the number of oxygen atoms) on the two sides are equal. The half-reaction is now complete and balanced.

Repeat these 4 steps for the other reactant/product pair.

Step 1: $Cu \longrightarrow Cu(H_2O)_6^{+2}$

Step 2: $Cu \longrightarrow Cu(H_2O)_6^{+2} + 2\ e^-$

Step 3: $Cu \longrightarrow Cu(H_2O)_6^{+2} + 2\ e^-$ Charge balanced!

Step 4: $6\ H_2O + Cu \longrightarrow Cu(H_2O)_6^{+2} + 2\ e^-$

Combine the two half-reactions to derive the balanced redox equation

$$2\ x\ [4\ H_3O^+ + 3\ e^- + NO_3^- \longrightarrow NO + 6\ H_2O]$$

$$+\ 3\ x\ [6\ H_2O + Cu \longrightarrow Cu(H_2O)_6^{+2} + 2\ e^-]$$

$$8\ H_3O^+ + 3\ Cu + 6\ H_2O + 2\ NO_3^- \longrightarrow 2\ NO + 3\ Cu(H_2O)_6^{+2}$$

Example 2: When concentrated nitric acid and concentrated hydrochloric acid are mixed, both chlorine gas and orange-colored nitrosyl chloride (NOCl) are formed. Derive both half-reactions and the net redox equation (and see why aqua regia is made by mixing them in a 1:3 ratio).

First, balance the Cl^-/Cl_2 reactant/product pair.

Step 1: $2\ Cl^- \longrightarrow Cl_2$

Step 2: $2\ Cl^- \longrightarrow Cl_2 + 2\ e^-$

Next, balance the NO_3^-, Cl^-/ NOCl reactant/product pair.

Step 1: $NO_3^- + Cl^- \longrightarrow NOCl$

Step 2: $2\ e^- + NO_3^- + Cl^- \longrightarrow NOCl$

Step 3: $4\ H_3O^+ + 2\ e^- + NO_3^- + Cl^- \longrightarrow NOCl$

Step 4: $4\ H_3O^+ + 2\ e^- + NO_3^- + Cl^- \longrightarrow NOCl + 6\ H_2O$

The net redox equation is:

$$
\begin{array}{rcl}
2\ Cl^- & \longrightarrow & Cl_2 + 2\ e^- \\
4\ H_3O^+ + 2\ e^- + NO_3^- + Cl^- & \longrightarrow & NOCl + 6\ H_2O \\
\hline
4\ H_3O^+ + NO_3^- + 3\ Cl^- & \longrightarrow & NOCl + 6\ H_2O + Cl_2
\end{array}
$$

NOTE THE 1:3 RATIO OF NO_3^- TO Cl^-!

REDOX HOMEWORK PROBLEMS

Balance the following reactions using the half reaction method.

1. When 1M H_2SO_4 is added to red Cu_2O, metallic copper and cupric ions are formed.

2. When 2M HNO_3 is added to Cu_2O, cupric ions and hydrogen gas are formed.

3. Zinc metal dissolves in 6M HNO_3 to give ammonium ions as one product.

4. Hydrogen peroxide oxidizes the chromite ion, $Cr(H_2O)_2(OH)_4^-$, to the chromate ion, CrO_4^{-2}. The product from hydrogen peroxide is OH^-.

5. Silver metal dissolves in 6M HNO_3 to give $Ag(H_2O)_2^+$ and NO as products.

6. Aluminum metal dissolves in 6M NaOH to produce hydrogen gas and $Al(H_2O)_2(OH)_4^-$.

7. When silver nitrate solution and iron(II) sulfate solution are mixed, metallic silver and iron(III) ions are produced.

REDOX HOMEWORK ANSWER KEY

1.

$$9\ H_2O + Cu_2O + 2\ H_3O^+ \longrightarrow 2\ Cu(H_2O)_6^{+2} + 2\ e^-$$

$$2\ H_3O^+ + Cu_2O + 2\ e^- \longrightarrow 2\ Cu + 3\ H_2O$$

$$6\ H_2O + 2\ Cu_2O + 4\ H_3O^+ \longrightarrow 2\ Cu(H_2O)_6^{+2} + 2\ Cu$$

2.

$$9\ H_2O + Cu_2O + 2\ H_3O^+ \longrightarrow 2\ Cu(H_2O)_6^{+2} + 2\ e^-$$

$$2\ H_3O^+ + 2\ e^- \longrightarrow H_2 + 2\ H_2O$$

$$7\ H_2O + Cu_2O + 4\ H_3O^+ \longrightarrow 2\ Cu(H_2O)_6^{+2} + H_2$$

3.

$$4 \times [Zn + 6\ H_2O \longrightarrow Zn(H_2O)_6^{+2} + 2\ e^-]$$

$$NO_3^- + 8\ e^- + 10\ H_3O^+ \longrightarrow NH_4^+ + 13\ H_2O$$

$$4\ Zn + 11\ H_2O + 10\ H_3O^+ + NO_3^- \longrightarrow 4\ Zn(H_2O)_6^{+2} + NH_4^+$$

4.

$$2 \times [Cr(H_2O)_2(OH)_4^- + 4\ OH^- \longrightarrow CrO_4^{-2} + 3\ e^- + 6\ H_2O]$$

$$3 \times [H_2O_2 + 2\ e^- \longrightarrow 2\ OH^-]$$

$$2\ Cr(H_2O)_2(OH)_4^- + 3\ H_2O_2 + 2\ OH^- \longrightarrow 2\ CrO_4^{-2} + 12\ H_2O$$

5.

$$3 \times [Ag + 2\ H_2O \longrightarrow Ag(H_2O)_2^+ + e^-]$$

$$4\ H_3O^+ + NO_3^- + 3\ e^- \longrightarrow NO + 6\ H_2O$$

$$3\ Ag + 4\ H_3O^+ + NO_3^- \longrightarrow 3\ Ag(H_2O)_2^+ + NO$$

6.

$$2 \times [Al + 4\ OH^- + 2\ H_2O \longrightarrow Al(H_2O)_2(OH)_4^- + 3\ e^-]$$

$$3 \times [2\ H_2O + 2\ e^- \longrightarrow 2\ OH^- + H_2]$$

$$2\ Al + 2\ OH^- + 10\ H_2O \longrightarrow 2\ Al(H_2O)_2(OH)_4^- + 3\ H_2$$

7.

$$Fe(H_2O)_6^{+2} \longrightarrow Fe(H_2O)_6^{+3} + e^-$$

$$Ag(H_2O)_2^+ + e^- \longrightarrow Ag + 2\ H_2O$$

$$Ag(H_2O)_2^+ + Fe(H_2O)_6^{+2} \longrightarrow Fe(H_2O)_6^{+3} + Ag + 2\ H_2O$$