3.1 - REDOX in Outline

Electron transfer reactions are collectively known as reduction-oxidation or REDOX reaction. No substance is ever oxidized unless something else is reduced. Otherwise, electrons would appear as a product of the reaction, which is never observed. An electron accepting substance is called the **oxidizing agent** because it helps something else to be oxidized. The substance that supplies the electrons is called the **reducing agent** because it helps something else to be reduced. An easy way to remember which element is being oxidized or reduced is by placing the numbers in a number line

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< (-)-(-4)-(-3)-(-2)-(-1)-0-(+1)-(+2)-(+3)-(+4)-(+) >
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The word "reduction" has the meaning you would expect from the number line. The word means **reducing the value or moving towards the negative side of the number line**.

Example 3.1a

Identify the element that is reduced and the element that is oxidized during the formation of Magnesium Oxide. Recall that elements in their pure form have a 0 (zero) oxidation state.

$$2Mg + O_2 \rightarrow 2MgO$$

First we write the half reactions:

$Mg^0 \rightarrow Mg^{2+} + 2e^-$

$O_2 + 4e^- \rightarrow O^{2-}$

Oxygen goes from 0 to 2-. Thus it moved towards the negative side of the number line and then the element that was REDUCED. Since electrons are negative, adding electrons makes the oxidation number smaller.

Magnesium moves from 0 to 2+. Thus it moved towards the positive side of the number line and was OXIDIZED. Since electrons are negative, removing electrons makes the oxidation number larger.

Thus we now know that the oxidation numbers behave just like simple arithmetic. If you add a minus one (1-) to a number it will become smaller, if you add an electron (e^-) to an element its oxidation number will become smaller.

There are six main rules for assigning oxidation numbers. The order in which these rules are written is very important because if two of them contradict each other then the last one listed takes precedence.

Rule 1. All pure substances have an oxidation number of zero. This applies to any pure substance whether it is a diatomic gas like O_2 or a piece of pure metal like Iron (Fe). Examples of

Rule 2. In compounds, elements that usually have an ionic charge imparted by their position in a particular group have that same oxidation number. An example is Cl which is usually in the form Cl^- in compounds; this will have an oxidation number of -1 in compounds.

Rule 3. When two or more usually negatively charged ions are involved in a compound, the one with the **highest electronegativity value** is given its ionic charge as the oxidation number; the others are worked out normally. An example is OF_2. F is more electronegative, and so it is assigned the value of -1.

Rule 4. Oxygen in a compound always has an oxidation number of -2

Rule 5. Hydrogen in compounds always has an oxidation number of +1 except in the rare case of Metal Hydrides where it has a value of -1.

Rule 6. The oxidation numbers in the compound or molecule must total to the **overall charge** of that compound or molecule. For example CO_2 has no overall charge and so the oxidation numbers must tally to zero. The sulfate ion, SO_4^{2-}, has an overall charge of -2, so the oxidation numbers must tally to -2.

Example 3.1b
Find the oxidation numbers in the elements from CH_2Cl_2

Rule 2: Cl has on oxidation number of -1
Rule 5: Hydrogen has an oxidation number of +1. This is not a metal hydride so the exception does not apply.
Rule 6: The sum of oxidation numbers must add up to the charge of the molecule

$C + 2Cl^- + 2H^+ = 0$
$X + (2-) + (2+) = 0$
$X = 0 + (+2) + (-2)$
$X = 0$

Thus the oxidation number of Carbon in CH2Cl2 is 0.

Example 3.1c
Find the oxidation numbers in the elements from H_2O_2

Rule 4: Oxygen in a compound always have an oxidation number of -2
Rule 5: Hydrogen has an oxidation number of +1. This is not a metal hydride so the exception does not apply.

The two rules contradict each other because if we use +1 for hydrogen and -2 for oxygen we get:
$2H^+ + 2O^{-2} = -2$

Thus we eliminate rule number 4 and keep rule number 5 (Hydrogen is +1).
Add rule number 6 (all oxidation numbers add up to the molecule's charge)
$2H^+ + 2O^{-x} = 0$
$2 + 2X = 0 \rightarrow 2X = 0 - 2 \rightarrow X = -1$
Thus the oxidation number of oxygen in H_2O_2 is -1.

3.2 – Balancing REDOX equations (Ion-Electron method)

In the Ion-Electron method, the reaction is divided into half reactions. For the reaction of Fe^{3+} and Sn^{2+} we have,

$$Fe^{3+} + Sn^{2+} \rightarrow Fe^{2+} + Sn^{4+}$$

First we write the half reactions: the oxidation of Tin and the reduction of iron,

$$Sn^{2+} \rightarrow Sn^{4+}$$

$$Fe^{3+} \rightarrow Fe^{2+}$$

Next, we balance the atoms and the charge. For this reaction, the atoms are balanced (one tin on both sides and one iron on both sides)

$$Sn^{2+} \rightarrow Sn^{4+} + 2e-$$

$$Fe^{3+} + e- \rightarrow Fe^{2+}$$

Now we balance the combined equations so that the number of electrons gained in the reduction reaction is the same as the number of electrons lost in the oxidation reaction.

$$Sn^{2+} \rightarrow Sn^{4+} + 2e-$$

$$(Fe^{3+} + e- \rightarrow Fe^{2+}) \text{ X } 2$$

Because each tin looses two electrons and each iron gains one electron, the iron reduction is multiplied by 2. The combined reactions yield the final balanced equation,

$$2Fe^{3+} + 2e- + Sn^{2+} \rightarrow 2Fe^{2+} + Sn^{4+} + 2e-$$

$$2Fe^{3+} + Sn^{2+} \rightarrow 2Fe^{2+} + Sn^{4+}$$

The previous REDOX looks so simple that it makes one wonder why we even bother going through all those steps. The answer is that not all reactions are so simple and most of the time it is necessary to through all those steps to balance a REDOX.

Half-Reactions Outline:

Reductant → Products + e

Loss of electrons (Oxidation Number increases)

Oxidant + e → Products

Gain of electrons (Oxidation Number decreases)

Example 3.2a

Balance the redox reaction between Gold 3+ and the Iodide ion.

$Au^{3+}(aq) + I^{-}(aq) \rightarrow Au(s) + I_2(s)$

The balanced half-reactions are:

$2I^{-}(aq) \rightarrow I_2(s) + 2e^{-}$

$Au^{3+}(aq) + 3e^{-} \rightarrow Au(s)$

Make electrons gained equal to electrons lost:

$3(\ 2I^{-}(aq) \rightarrow I_2(s) + 2e^{-}\ )$

$2(\ Au^{3+}(aq) + 3e^{-} \rightarrow Au(s)\ )$

Add the half-reactions:

$2Au^{3+}(aq) + 6e^{-} + 6I^{-}(aq) \rightarrow 3I_2(s) + 6e^{-} + 2Au(s)$

Cancel anything that is the same on both sides:

$2Au^{3+}(aq) + 6I^{-}(aq) \rightarrow 3I_2(s) + 2Au(s)$

Example 3.2b

Balance the following redox reaction.

$SnCl_3^{-}(aq) + HgCl_2(aq) \rightarrow SnCl_6^{2-}(aq) + Hg_2Cl_2(s)$

The balanced half-reactions are:

$SnCl_3^{-}(aq) + 3Cl^{-} \rightarrow SnCl_6^{2-} + 2e^{-}$

$2HgCl_2 + 2e^{-} \rightarrow Hg_2Cl_2 + 2Cl^{-}$

Make electrons gained equal to electrons lost:

$SnCl_3^{-}(aq) + 3Cl^{-} \rightarrow SnCl_6^{2-} + 2e^{-}$

$HgCl_2 + 2e^{-} \rightarrow Hg_2Cl_2 + 2Cl^{-}$

Electrons are balanced

Add the half-reactions:

$SnCl_3^{-}(aq) + 3Cl^{-} + 2HgCl_2 + 2e^{-} \rightarrow SnCl_6^{2-} + 2e^{-} + Hg_2Cl_2 + 2Cl^{-}$

Cancel anything that is the same on both sides:

$SnCl_3^{-}(aq) + Cl^{-} + 2HgCl_2 \rightarrow SnCl_6^{2-} + Hg_2Cl_2$

3.3 – Ion-Electron method for reactions involving OH^- and H^+.

Redox reactions are commonly run in acidic solution, in which case the reaction equations often include $H_2O(l)$, $OH^-(aq)$ and $H^+(aq)$ but you might not know whether the $H_2O(l)$), $OH^-(aq)$ and $H^+(aq)$ are reactants or products. For example, you may know that dichromate ions, $Cr_2O_7^{2-}$, react with nitrous acid molecules, HNO_2, in acidic conditions to form chromium ions, Cr^{3+}, and nitrate ions, NO_3^-. Because the reaction requires acidic conditions, you assume that $H_2O(l)$ and $H^+(aq)$ participate in some way, but you do not know whether they are reactants or products, and you do not know the coefficients for the reactants and products. An unbalanced equation for this reaction might be written

$$Cr_2O_7^{2-}(aq) + HNO_2(aq) \rightarrow Cr^{3+}(aq) + NO_3^-(aq) \qquad \text{(acidic solution)}$$

In order to balance equations of this type, we need to add more steps to the ion-electron method. Note we have added steps 2, 3, and 4.

Ion-Electron method Outline

[1] Divide equation into half-reaction
[2] Balance atoms other than H and O
[3] Balance O by adding H_2O
[4] Balance H by adding H^+
[5] Balance net charge by adding e^-
[6] Make e^- gain equal to e^- loss and add half reactions
[7] Add half reactions and cancel anything that is the same on both sides

For Basic solution add steps

[8] Add to both sides of the equation the same number of OH^- as there are H^+.
[9] Combine OH^- and H^+ to form H_2O.
[10] Cancel any H_2O that you can.

Example 3.3a

Balance the following redox equation using the half-reaction method in acidic solution.

$$Cr_2O_7^{2-}(aq) + HNO_2(aq) \text{ --> } Cr^{3+}(aq) + NO_3^-(aq)$$

Separate the two half reactions:

$$Cr_2O_7^{2-} \rightarrow Cr^{3+}$$
$$HNO_2 \rightarrow NO_3^-$$

Balance atoms other than H and O

$$Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$$
$$HNO_2 \rightarrow NO_3^-$$

Add water to balance O

$$Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$$
$$HNO_2 + H_2O \rightarrow NO_3^-$$

Add H^+ to balance H:

$$Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$$
$$HNO_2 + H_2O \rightarrow NO_3^- + 3H^+$$

Balance net charge by adding e^-

$$6e^- + Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$$
$$HNO_2 + H_2O \rightarrow NO_3^- + 3H^+ + 2e^-$$

Make e^- gain equal to e^- loss and add half reactions

$$6e^- + Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$$
$$3(HNO_2 + H_2O \rightarrow NO_3^- + 3H^+ + 2e^-)$$

$$6e^- + Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$$
$$3HNO_2 + 3H_2O \rightarrow 3NO_3^- + 9H^+ + 6e^-$$

Add half reactions and cancel anything that is the same on both sides

$$6e^- + Cr_2O_7^{2-} + 14H^+ + 3HNO_2 + 3H_2O \rightarrow 2Cr^{3+} + 7H_2O + 3NO_3^- + 9H^+ + 6e^-$$

3 H_2O in the second half-reaction cancel three of the 7 H_2O in the first half-reaction
9 H^+ on the right of the second half-reaction cancel nine of the 14 H^+ on the left of the first half-reaction

$$Cr_2O_7^{2-} + 5H^+ + 3HNO_2 \rightarrow 2Cr^{3+} + 4H_2O + 3NO_3^-$$

Check to make sure that the atoms and the charge are balanced.
The atoms in this example balance and the sum of the charges is +3 on each side, so the equation is correctly balanced.

Example 3.3b
Balance the redox reaction between MnO_4^- and I^- in acidic then basic.

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$$MnO_4^- + I^- \longrightarrow I_2 + Mn^{2+}$$

Separate the two half reactions:

$$I^- \rightarrow I_2$$
$$MnO_4^- \rightarrow Mn^{2+}$$

Balance the iodine atoms:

$2I^- \rightarrow I_2$

The Mn in the permanganate reaction is already balanced, so let's balance the oxygen:

$MnO_4^- \rightarrow Mn^{2+} + 4H_2O$

Add H^+ to balance the 4 waters molecules:

$MnO_4^- + 8\ H^+ \rightarrow Mn^{2+} + 4H_2O$

Next, balance the charges in each half-reaction so that the reduction half-reaction consumes the same number of electrons as the oxidation half-reaction supplies. This is accomplished by adding electrons to the reactions:

$2\ I^- \rightarrow I_2 + 2e^-$

$5\ e^- + 8\ H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O$

Now multiple the oxidations numbers so that the two half-reactions will have the same number of electrons and can cancel each other out:

$5(2I^- \rightarrow I_2 + 2e^-)$

$2(5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O)$

Now add the two half-reactions:

$10\ I^- \rightarrow 5I_2 + 10\ e^-$

$16\ H^+ + 2MnO_4^- + 10\ e^- \rightarrow 2Mn^{2+} + 8H_2O$

This yields the following final equation:

$10\ I^- + 10\ e^- + 16\ H^+ + 2\ MnO_4^- \rightarrow 5\ I_2 + 2Mn^{2+} + 10\ e- + 8H_2O$

Get the overall equation by canceling out the electrons and H2O, H+, and OH- that may appear on both sides of the equation:

$10I^- + 16H^+ + 2MnO_4^- \rightarrow 5I_2 + 2Mn^{2+} + 8H_2O$

For the reaction in basic solution,
Add $16OH^-$ on both sides

$16OH^- + 10I^- + 16H^+ + 2MnO_4^- \rightarrow 5I_2 + 2Mn^{2+} + 8H_2O + 16OH^-$

Combine $16OH^-$ and $16H^+$ to form $16H_2O$

$16H_2O + 10I^- + 2MnO_4^- \rightarrow 5I_2 + 2Mn^{2+} + 8H_2O + 16OH^-$

Cancel any H_2O that you can

$8H_2O + 10I^- + 2MnO_4^- \rightarrow 5I_2 + 2Mn^{2+} + 16OH^-$