Chapter 4: Oxidation-Reduction

Section 4.1: Introduction to Oxidation and Reduction Reactions

Oxidation-reduction reactions are chemical reactions involving the exchange of electrons between two substances.

During an **oxidation** reaction, there is a loss of electrons. For example, the oxidation of $Fe_{(s)}$ to $Fe^{+2}_{(aq)}$ is accompanied by the loss of two electrons. This reaction is represented by the net ionic equation:

$$Fe_{(s)} \rightarrow Fe^{+2}_{(aq)} + 2\ e^{-}$$

During a **reduction** reaction, there is a gain of electrons. For example, the reduction of $Cu^{+2}_{(aq)}$ to $Cu_{(s)}$ is accompanied by the gain of two electrons. This reaction is represented by the net ionic equation:

$$Cu^{+2}_{(aq)} + 2\ e^{-} \rightarrow Cu_{(s)}$$

To remember that **O**xidation **I**s the **L**oss of electrons (electrons on the right-hand side of the equation) and that **R**eduction **I**s the **G**ain of electrons (electrons on the left-hand side of the equation), remember **OIL-RIG**.

Oxidation and reduction occur together. Hence, they are called **redox** reactions. In a redox reaction, one substance gains electrons (undergoing a reduction), while the other substance loses electrons (undergoing an oxidation).

For instance, consider the following redox reaction:

$$Cu^{+2}_{(aq)} + Fe_{(s)} \rightarrow Fe^{+2}_{(aq)} + Cu_{(s)}$$

In this reaction, $Cu^{+2}_{(aq)}$ is reduced to $Cu_{(s)}$ and $Fe_{(s)}$ is simultaneously oxidized to $Fe^{+2}_{(aq)}$.

The substance undergoing reduction (substance being reduced) is called the **oxidizing** agent. The substance undergoing oxidation (substance being oxidized) is called the **reducing** agent.

A typical redox reaction is represented as:

OXIDIZING AGENT		REDUCED FORM OF OXIDIZING AGENT
+	→	+
REDUCING AGENT		OXIDIZED FORM OF REDUCING AGENT

Considering the same redox reaction as above:

$$Cu^{+2}_{(aq)} + Fe_{(s)} \rightarrow Fe^{+2}_{(aq)} + Cu_{(s)}$$

The oxidizing agent is $Cu^{+2}_{(aq)}$
The reducing agent is $Fe_{(s)}$
The reduced form of the oxidizing agent is: $Cu_{(s)}$
The oxidized form of the reducing agent is: $Fe^{+2}_{(aq)}$

How can we tell if a given chemical reaction is a redox reaction?

For some reactions, it is simple. Any reaction where a given element is combined with a different number of oxygen atoms on the reactants side and on the products side is a redox reaction.

For example, consider the reaction:

$$2\ Al_{(s)} + Fe_2O_{3\ (s)} \rightarrow Al_2O_{3\ (s)} + 2\ Fe_{(s)}$$

The ratio of oxygen to aluminum is higher on the product side (3 "O" for 2 "Al") than on the reactant side (0 "O" for 2 "Al"). Hence, aluminum is more oxidized in $Al_2O_{3\ (s)}$ than in the elemental state, $Al_{(s)}$. We say that aluminum undergoes an oxidation in this reaction. In contrast, you can see that iron is more oxidized in $Fe_2O_{3\ (s)}$ than in the elemental state, $Fe_{(s)}$. Hence, iron undergoes a reduction in this reaction.

However, there will be many reactions where it is more difficult to determine whether a given substance undergoes reduction or oxidation. In order to help us answer this question, we will learn to calculate **oxidation numbers**.

The oxidation number is a number which tells us how oxidized or reduced a given element of a given substance is. The higher the oxidation number is, the more oxidized the element is. Oxidation number will also help us greatly with the bookkeeping of electrons in reduction or oxidation reactions.

Section 4.2: Rules for Assigning Oxidation Numbers (11 rules)

Rule #1: The oxidation number for an element in the elemental state is 0.

For example, in the above reaction, the oxidation numbers for Al in $Al_{(s)}$ and for Fe in $Fe_{(s)}$ are both 0.

Rule #2: The oxidation number for any monoatomic ion is the charge of the ion.

For example, in the reaction: $Cu^{+2}_{(aq)} + Fe_{(s)} \rightarrow Fe^{+2}_{(aq)} + Cu_{(s)}$, the oxidation numbers for Cu in $Cu^{+2}_{(aq)}$ and for Fe in $Fe^{+2}_{(aq)}$ are both equal to **+2**.
The oxidation number of Fe in $Fe^{+3}_{(aq)}$ is **+3**.
The oxidation number of N in $N^{-3}_{(aq)}$ is **- 3**.
The oxidation number of S in $S^{-2}_{(aq)}$ is **-2**.
The oxidation number of Cl in $Cl^{-}_{(aq)}$ is **-1**.

Rule #3: The oxidation number for oxygen in most oxygen compounds (excluding peroxides and superoxides, a minor fraction of oxygen compounds) is equal to - 2.

Rule #4: In all group I compounds, the oxidation number of the metal element is +1. (does not apply to H, since it is not a metal)

Na in $NaCl_{(s)}$ or in $Na_2SO_{4(s)}$ has an oxidation number of +1

Rule #5: In all group II compounds, the oxidation number of the metal is +2.

Ca in $CaCO_3$ and in $Ca(NO_3)_2$ has an oxidation number of +2

Rule #6: In all fluorine compounds, the oxidation number of fluorine is -1.

The oxidation number of F in NaF, CaF_2 and AlF_3 is always -1.

Rule #7: In all Cl, Br, I compounds, the oxidation number of the halogen is -1, unless the halogen is combined with oxygen or with another halogen.

In NaCl, Cl has an oxidation number of -1.
In BrCl, Br has an oxidation number of +1 and Cl has an oxidation number of -1.
Note the second halogen in the formula (Cl) plays the role of a nonmetal (oxidation number is -1 in this case, as for F another halogen), while the first halogen in the formula (Br) plays the role of a metal cation (positive oxidation number).

Rule #8: In a compound, the oxidation number of hydrogen is +1 if H is bonded to a nonmetal.

H in NH_3, in CH_4, in H_2O and in HCN has the same oxidation number of +1.

Rule #9: In a compound, the oxidation number of hydrogen is -1 if H is bonded to a metal. (Note: in this case, H behaves like an anion and is called hydride)

H in NaH (sodium hydride), in CaH_2 (calcium hydride) has the oxidation number of -1.

Rule #10: The sum of the oxidation numbers of all elements in a compound is equal to 0 (the charge of the compound).

For example in NO_2, oxidation #(nitrogen) + 2 x oxidation #(oxygen) = 0.
We will write this symbolically as: “N” + 2 “O” = 0

Rule #11: The sum of the oxidation numbers of all elements in a polyatomic ion is equal to the charge of the polyatomic ion.

For example in CO_3^{-2}, oxidation #(carbon) + 3 x oxidation #(oxygen) = -2.
We will write this symbolically as: "C" + 3 "O" = -2

Section 4.3: Assigning Oxidation Numbers

In this section we apply the above 11 rules to calculate the oxidation number of an element in a compound. Note that many elements can have very different values of the oxidation number.

Consider Na_2SO_4:

Oxidation number of Na = "Na" = +1
Oxidation number of O = "O" = -2
Oxidation number of S: = "S" to be calculated
2 "Na" + "S" + 4 "O" = 0
2x(+1) + "S" + 4x(-2) = 0
"S" – 6 = 0
"S" = +6

Consider SO_3^{-2}:

"S" + 3x(-2) = -2
"S" = +4

Consider S^{-2}:

"S" = -2

Consider S_8:

"S" = 0

Consider $H_2PO_4^-$:

Oxidation number of H = "H" = +1
Oxidation number of O = "O" = -2
Oxidation number of P: = "P" to be calculated
2 "H" + "P" + 4 "O" = -1
2x(+1) + "P" + 4x(-2) = -1
"P" – 6 = -1
"P" = +5

Section 4.4: Assigning Oxidation Numbers (Interactive)

Practice, practice, practice.

Section 4.5: Balancing Half-reactions (Oxidation and Reduction)

In this section we use our understanding of oxidation numbers to balance redox reactions. We need to emphasize at the onset that when balancing redox reactions, it is much easier to start by balancing the reduction half-reaction and the oxidation half-reaction (called half-reactions because any redox reaction has two parts: oxidation and reduction).

We will start with the simple case where the half-reaction involves only one element, as in the case:

$$Fe_{(s)} \rightarrow Fe^{+2}_{(aq)} + 2\ e^{-}$$

To balance such reaction equation, we only need to balance:

1) the element involved,

2) the oxidation number.

When we write: $Fe_{(s)} \rightarrow Fe^{+2}_{(aq)}$ we have actually already balanced the equation as far as the element iron is concerned (1 on each side of the equation).
Next, we need to balance the equation as far oxidation number is concerned. Since Fe has an oxidation number equal to 0 on the left-hand side of the equation and an oxidation number of +2 on the right-hand side, we add two electrons on the right-hand side to get the fully balanced half-reaction:

$$Fe_{(s)} \rightarrow Fe^{+2}_{(aq)} + 2\ e^{-}$$

Similarly, consider the oxidation half-reaction of $Hg_{(l)}$ to $Hg_2^{+2}{}_{(aq)}$.
The oxidation half-reaction is written in balanced form as:

$$2\ Hg_{(l)} \rightarrow Hg_2^{+2}{}_{(aq)} + 2\ e^{-}$$

You can also consider the reduction of chlorine gas to chloride ion as:

$$Cl_{2\ (g)} + 2\ e^{-} \rightarrow 2\ Cl^{-}_{(aq)}$$

The above cases were very simple as only one element was involved in each half-reaction.

What should be done if more than one element is involved in a half-reaction?
Consider for example the following half-reaction involving manganese and oxygen:

$$MnO_4^{-}{}_{(aq)} \rightarrow Mn^{+2}_{(aq)}$$

To balance this and similar half-reactions we need to follow these four steps.

<u>STEP 1</u>: Balance the element being oxidized or reduced.

Obviously, you need to be sure which element is being oxidized or reduced. In the above half-reaction, Mn is being reduced, since its oxidation number decreases from the value of +7 in $MnO_4^-{}_{(aq)}$ to the value of +2 in $Mn^{+2}{}_{(aq)}$.
The half-reaction: $MnO_4^-{}_{(aq)} \rightarrow Mn^{+2}{}_{(aq)}$ is already balanced for Mn.

<u>STEP 2</u>: Balance the oxidation number by adding the appropriate number of electrons on the appropriate side of the half-reaction.

Manganese has an oxidation number of +7 on the left-hand side and an oxidation number of +2 on the right hand side. Hence, this reaction is a reduction half-reaction and 5 electrons ((+7) – (+2) = 5) must be added on left-hand side of the half-reaction.

$$MnO_4^-{}_{(aq)} + 5\ e^- \rightarrow Mn^{+2}{}_{(aq)}$$
$$+7 \quad - \quad 5 \quad = \quad +2$$

<u>STEP 3</u>: Balance the charges by adding the appropriate number of H^+ on the appropriate side of the reaction when the reaction is run in acidic conditions, or, add the appropriate number of OH^- on the appropriate side of the reaction when the reaction is run in basic conditions.

Whether a reaction is run under acidic or basic conditions is always given in the problem of interest.
The reaction balanced up to step 2 is such that there are <u>6 negative charges</u> on the LHS of the equation and <u>2 positive charges</u> on the RHS of the equation.

Acidic Conditions:
We add H^+ to balance the charges. Since there is a differential of 8 charges between the LHS and the RHS, we must add 8 H^+ on the left-hand side of the equation to balance the charges.

The oxidation half-reaction becomes:

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

Basic Conditions:
We add OH^- to balance the charges. Since there is a differential of 8 charges between the LHS and the RHS, we must add 8 OH^- on the right-hand side of the equation to balance the charges. The oxidation half-reaction becomes:

$$MnO_4^-{}_{(aq)} + 5\ e^- \rightarrow Mn^{+2}{}_{(aq)} + 8\ OH^-{}_{(aq)}$$

<u>STEP 4</u>: Balance the elements hydrogen and oxygen by adding the appropriate number of H_2O molecules on the appropriate side of the half-reaction.

If adding the appropriate number of H_2O molecules does not lead to a fully balanced reaction, then, you must have made a mistake along the way.

Acidic Conditions: You need to add 4 H_2O molecules on the RHS of the equation to get the fully balanced half-reaction:

$$MnO_4^-{}_{(aq)} + 8\ H^+{}_{(aq)} + 5\ e^- \rightarrow Mn^{+2}{}_{(aq)} + 4\ H_2O_{(l)}$$

Basic Conditions: You need to add 4 H_2O molecules on the LHS of the equation to get the fully balanced half-reaction:

$$MnO_4^-{}_{(aq)} + 4\ H_2O_{(l)} + 5\ e^- \rightarrow Mn^{+2}{}_{(aq)} + 8\ OH^-{}_{(aq)}$$

Once, you have balanced the oxidation half-reaction and the reduction half-reaction, you only need to learn how to combine these half-reactions into the full redox reaction (section 4.9).

Before moving to the "Interactive Sections on Balancing Half-Reactions", you may also want to consider the following case, which involves two substances containing different numbers of the element undergoing oxidation or reduction.

Let us consider the oxidation half-reaction involving the following substances:

$$\mathbf{Al_2(Cr_2O_7)_{3\ (s)} \rightarrow CrCl_{2\ (s)}}\quad \textbf{(in acidic medium)}$$

When balancing half-reactions involving ionic compounds, we only concern ourselves with the monoatomic ions or polyatomic ions containing the element involved in the redox process.

In the above reaction, we see that the element chromium is involved in two compounds having different ratios of chromium to oxygen. Hence, chromium is the element involved in the redox process. We will therefore only focus on the ions, $Cr_2O_7^{-2}$ and Cr^{+2}. Hence, we start writing the half-reaction as:

$$Cr_2O_7^{-2}{}_{(aq)} \rightarrow Cr^{+2}{}_{(aq)}$$

STEP 1: Balance the element.

$$Cr_2O_7^{-2}{}_{(aq)} \rightarrow 2\ Cr^{+2}{}_{(aq)}.$$

STEP 2: Balance the oxidation numbers.

The oxidation number of Cr is +6 in $Cr_2O_7^{-2}$ and is +2 in Cr^{+2}. Difference of 4 ((+6) – (+2)). However, this difference is for one Cr atom. Here, we have two Cr atoms. Hence, 8 electrons must be added on the left-hand side.

$$Cr_2O_7^{-2}{}_{(aq)} + 8\ e^- \rightarrow 2\ Cr^{+2}{}_{(aq)}$$

STEP 3: Balance the charges assuming an acidic medium.

There are 10 negative charges on the left-hand side and 4 positive charges on the right-hand side. Hence, we must add 14 H^+ ions on the left-hand side to balance the charges (acidic medium).

$$Cr_2O_7^{-2}{}_{(aq)} + 8\ e^- + 14\ H^+{}_{(aq)} \rightarrow 2\ Cr^{+2}{}_{(aq)}$$

STEP 4: Balance the elements Hydrogen and Oxygen by adding water.

To balance hydrogen and oxygen, we only need to add 7 H_2O on the right-hand side. The fully balanced half-reaction is written as:

$$Cr_2O_7^{-2}{}_{(aq)} + 8\ e^- + 14\ H^+{}_{(aq)} \rightarrow 2\ Cr^{+2}{}_{(aq)} + 7\ H_2O_{(l)}$$

Sections 4.6 - 4.8: Balancing Half-Reactions (Interactive)

Practice balancing half-reactions under acidic and basic conditions using these guided Interactive Problems.

Sections 4.9 - 4.11: Balancing Overall Redox Reaction Equations

In this section, we use the results obtained in Section 4.5 (balancing half-reactions) to balance an overall redox reaction. The strategy for balancing an overall redox reaction is best understood through an example.

Let us consider the following redox reaction:

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

Balancing the overall reaction is done in FOUR PARTS.

<u>PART I</u>: Split the redox equation into an OXIDATION HALF-REACTION and a REDUCTION HALF-REACTION.

Oxidation Half-Reaction: $Fe^{+2}{}_{(aq)} \rightarrow Fe^{+3}{}_{(aq)}$

Reduction Half-Reaction: $MnO_4^-{}_{(aq)} \rightarrow Mn^{+2}{}_{(aq)}$

<u>PART II</u>: Balance the OXIDATION HALF-REACTION.

Following the examples discussed in section 4.5, we write the balanced oxidation half-reaction as:

$$Fe^{+2}_{(aq)} \rightarrow Fe^{+3}_{(aq)} + e^-$$

<u>PART III</u>: Balance the REDUCTION HALF-REACTION.

Following the examples discussed in section 4.5, we write the balanced reduction half-reaction as:

$$MnO_4^-{}_{(aq)} + 8\ H^+{}_{(aq)} + 5\ e^- \rightarrow Mn^{+2}_{(aq)} + 4\ H_2O_{(l)}$$

Note that this reaction is fully balanced (Mn, H, and O elements, charges (+2 on each side)).

<u>PART IV</u>: Combine the OXIDATION and the REDUCTION HALF-REACTIONS.

Here, we combine the oxidation and the reduction half-reactions to obtain the equation for the full redox reaction. To do so, we need to ensure that <u>the same number of electrons is produced by the oxidation half-reaction and used up in the reduction half-reaction</u>. Since 5 electrons are used up by the reduction half-reaction, the oxidation half-reaction must be multiplied by 5 so that it produces 5 electrons.

$$5\ Fe^{+2}_{(aq)} \rightarrow 5\ Fe^{+3}_{(aq)} + 5\ e^-$$

5 e^- released by oxidation

$$MnO_4^-{}_{(aq)} + 8\ H^+{}_{(aq)} + 5\ e^- \rightarrow Mn^{+2}_{(aq)} + 4\ H_2O_{(l)}$$

5 e^- used up in reduction

We can now add the two half-reactions and obtain:

$$MnO_4^-{}_{(aq)} + 8\ H^+{}_{(aq)} + 5\ e^- + 5\ Fe^{+2}_{(aq)} \rightarrow 5\ Fe^{+3}_{(aq)} + 5\ e^- + Mn^{+2}_{(aq)} + 4\ H_2O_{(l)}$$

The redox equation is then simplified to yield the fully balanced equation (<u>for each element and for the charges</u>):

$$MnO_4^-{}_{(aq)} + 8\ H^+{}_{(aq)} + 5\ Fe^{+2}_{(aq)} \rightarrow 5\ Fe^{+3}_{(aq)} + Mn^{+2}_{(aq)} + 4\ H_2O_{(l)}$$

In Sections 4.10, 4.11, practice the Interactive Problems on balancing overall redox reaction equations under acidic or basic conditions.

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