Balancing REDOX Reactions: Learn and Practice

Reduction-Oxidation reactions (or REDOX reactions) occur when the chemical species involved in the reactions gain and lose electrons. Oxidation and reduction occur simultaneously in order to conserve charge. We can "see" these changes if we assign oxidation numbers to the reactants and products. For rules about assigning oxidation numbers, check the ebook's list of rules. In order to balance REDOX reactions well, you must first be able to assign oxidation numbers well.

Oxidation – The *loss* of electrons, resulting in a more *positively* charged species.

<u>Reduction</u> – The *gain* of electrons, resulting in a more *<u>negatively</u>* charged species.

When presented with a REDOX reaction in this class, we will use the "half-reactions" method to balance the reaction. Let's take a look at a simple reaction **WITHOUT HYDROGEN OR OXYGEN** to balance:

$$K(s) + Br_2(l) \rightarrow KBr(aq)$$

• First, is this even a REDOX reaction? Is there a species that is being reduced and a species that is being oxidized? We must assign oxidation numbers. A good way to start is to write out an ionic equation. We often remove the state symbols for clarity's sake.

Oxidation Numbers:
$$K + Br_2 \rightarrow K^+ + Br_2^-$$

- Yes, the potassium (K) has been oxidized and the bromine (Br) has been reduced.
- Now, we break the reaction into *two* half-reactions: the oxidation half-reaction and the reduction half-reaction.

Oxidation ½ Reaction:	$\mathbf{K}^{0} \rightarrow \mathbf{K}^{+}$
Reduction ½ Reaction:	$\operatorname{Br}_{2}^{0} \operatorname{Br}_{2}^{-}$

• Next, we balance all the elements in the half-reactions:

Oxidation ¹ / ₂ Reaction:	$K^0 \rightarrow K^+$
Reduction ¹ / ₂ Reaction:	$\operatorname{Br}_{2}^{0} \rightarrow 2\operatorname{Br}^{-}$

• Now, we balance all the charges in the half-reactions by adding electrons. Note that electrons are added to the products side in the oxidation half-reaction and to the reactants side in the reduction half-reaction. This should always be true.

Oxidation ¹ / ₂ Reaction:	$K^0 \rightarrow K^+ + 1e^-$
Reduction ¹ / ₂ Reaction:	$Br_2^0 + 2e^- \rightarrow 2Br^-$

• We would like to combine these two half-reactions into a final overall reaction. We must cancel out all the electrons because these are not part of our overall equation. Right now

if we tried to add our equations, we would be in trouble! The number of electrons on the reactants side (2e) is greater than the number of electrons on the products side (1e).

• So, we balance the half-reactions like an algebraic system of equations. Here, we will multiply everything in the oxidation half-reaction by 2 in order to bring the total number of electrons up to 2 electrons:

Oxidation ½ Reaction:	$2\mathbf{x}(\mathbf{K}^{0} \rightarrow \mathbf{K}^{+} + 1\mathbf{e}^{-})$
New Oxidation ½ Reaction:	$2K^0 \rightarrow 2K^+ + 2e^-$
Reduction ¹ / ₂ Reaction:	$Br_2^0 + 2e^- \rightarrow 2Br^-$
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• Now, combine the new half-reactions into a final equation. Note that all of the electrons have cancelled out:

New Oxidation ½ Reaction:	$2K^{0} \rightarrow 2K^{+} + 2e^{-}$	
Reduction ½ Reaction:	$+ Br_2^0 + 2e^- \rightarrow 2Br^-$	
Balanced Ionic Equation:	$2K^0 + Br_2^0 \rightarrow 2K^+ + 2Br^-$	

• Check that the charges on all the species are balanced. Remember to multiply the charges on a species by the coefficient! Here our reaction is balanced. We can fill-in our balanced coefficients to the original reaction from the problem:

Balanced Equation: $2K(s) + Br_2(l) \rightarrow 2KBr(aq)$

Practice:

Are these reactions are REDOX reactions? If yes, then balance the reaction using the half-reaction method.

1.
$$Au^{3+}(aq) + I^{-}(aq) \rightarrow Au(s) + I_{2}(s)$$

2.
$$Cu(s) + Ag^+(aq) \rightarrow Cu^{2+}(aq) + Ag(s)$$

3.
$$BaSO_3(s) \rightarrow BaO(s) + SO_2(g)$$

Great job. Now, we must consider more complicated REDOX reactions. Aqueous solutions in electrochemistry are often acidic or basic. The protons (H^+) and hydroxides (OH^-) contribute the balancing of chemical species and charge in our half-reactions. We will still follow a method of half-reactions, with just a bit more balancing.

Let's first consider *acidic* solutions:

$$\text{ClO}_3^-(\text{aq}) + \text{I}_2(\text{s}) \rightarrow \text{IO}_3^-(\text{aq}) + \text{Cl}^-(\text{aq})$$

(in acidic solution)

• First, is this even a REDOX reaction? Is there a species that is being reduced and a species that is being oxidized? We must assign oxidation numbers. A good way to start is to write out an ionic equation. Here, the equation is already written in an ionic equation format, so we must do some more work to assign oxidation numbers (see ebook rules).

 $\begin{array}{c} \text{CIO}_{3}^{-}(\text{aq}) + \text{I}_{2}(\text{s}) \rightarrow \text{IO}_{3}^{-}(\text{aq}) + \text{CI}^{-}(\text{aq})\\ \text{Oxidation Numbers:} \overset{+5-2}{\xrightarrow{}} \overset{-1}{\xrightarrow{}} \overset{-1}{\xrightarrow{}} \overset{-1}{\xrightarrow{}} \end{array}$

- Yes, the Iodine (I) has been oxidized and the Chlorine (Cl) has been reduced.
- Now, we break the reaction into *two* half-reactions:

Oxidation ¹ / ₂ Reaction:	$I_2 \rightarrow IO_3^-$
Reduction ½ Reaction:	$ClO_3^- \rightarrow Cl^-$

• Next, we balance all the elements **EXCEPT FOR Hydrogen and Oxygen**:

Oxidation ½ Reaction:	$I_2 \rightarrow 2IO_3^-$
Reduction ½ Reaction:	$ClO_3^- \rightarrow Cl^-$

• Now, to balance the **OXYGENS**, add water molecules to the half-reactions as needed:

Oxidation ½ Reaction:	$I_2 + 6H_2O \rightarrow 2IO_3^-$
Reduction ½ Reaction:	$\text{ClO}_3^- \rightarrow \text{Cl}^- + 3\text{H}_2\text{O}$

• Then, to balance the **HYDROGENS**, add protons (H⁺) to the half-reactions as needed:

Oxidation ¹ / ₂ Reaction:	$I_2 + 6H_2O \rightarrow 2IO_3^- + 12H^+$
Reduction ¹ / ₂ Reaction:	$ClO_3^- + 6H^+ \rightarrow Cl^- + 3H_2O$

• Next, we balance **CHARGE** by adding electrons. Remember to multiply the charges on a species by the coefficient! Note that electrons are added to the products side in the oxidation half-reaction and to the reactants side in the reduction half-reaction. This should always be true:

Oxidation ¹ / ₂ Reaction:	$I_2 + 6H_2O \rightarrow 2IO_3^- + 12H^+ + 10e^-$
Reduction ¹ / ₂ Reaction:	$\text{ClO}_3^- + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{Cl}^- + 3\text{H}_2\text{O}$

- We would like to combine these two half-reactions into a final overall reaction. We must cancel out all the electrons because these are not part of our overall equation. Right now if we tried to add our equations, we would be in trouble! The number of electrons on the reactants side (6e) is less than the number of electrons on the products side (10e).
- So, we balance the half-reactions like an algebraic system of equations. Here, we will multiply everything in the oxidation half-reaction by 3 and everything in the reduction reaction by 5 in order to bring the total number of electrons up to 30 electrons:

Oxidation ¹ / ₂ Reaction:	$3x(I_2 + 6H_2O \rightarrow 2IO_3^- + 12H^+ + 10e^-)$
New Oxidation ½ Reaction:	$3I_2 + 18H_2O \rightarrow 6IO_3^- + 36H^+ + 30^-$
Reduction ¹ / ₂ Reaction:	$5x(ClO_3^- + 6H^+ + 6e^- \rightarrow Cl^- + 3H_2O)$
New Reduction ½ Reaction	$: 5ClO_3^- + 30H^+ + 30e^- \rightarrow 5Cl^- + 15H_2O$

• Combine the new half-reactions. Note that all of the electrons have cancelled out:

New Oxidation ¹/₂ Reaction: $3I_2 + 18H_2O \rightarrow 6IO_3^- + 36H^+ + 30e^-$

<u>New Reduction ¹/₂ Reaction: + $5ClO_3^- + 30H^+ + 30e^- \rightarrow 5Cl^- + 15H_2O$ </u>

Overall Reaction: $3I_2 + 18H_2O + 5CIO_3^- + 30H^+ \rightarrow 6IO_3^- + 36H^+ + 5CI^- + 15H_2O$

• Continue to balance the reaction by reducing the number of water molecules and protons:

Balanced Equation: $3I_2 + 3H_2O + 5CIO_3^{-} \rightarrow 6IO_3^{-} + 6H^+ + 5CI^-$

• It is perfectly acceptable to have protons in our final balanced equation because we are in an acidic solution, which contains excess protons.

Practice:

Balance the following reactions using the half-reaction method in an *acidic* solution.

1. $NbO_2 + W \rightarrow Nb + WO_4^{2-}$

2.
$$C_2H_5OH(aq) + MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + CH_3COOH(aq)$$
 (Attempt this!)

3.
$$ClO^- + ZnO \rightarrow Cl^- + Zn^{3+}$$

Let's consider *basic* solutions:

The process for balancing will begin much in the same way as before.

$$Br_2(l) \rightarrow BrO_3^-(aq) + Br^-(aq)$$

(in basic solution)

• First, is this even a REDOX reaction? Is there a species that is being reduced and a species that is being oxidized? We must assign oxidation numbers. A good way to start is to write out an ionic equation. Here, the equation is already written in an ionic equation format, so we must do some more work to assign oxidation numbers (see ebook rules).

Oxidation Numbers:
$$Br_{2}(l) \rightarrow BrO_{3}^{-}(aq) + Br^{-}(aq)$$
$$\rightarrow^{+5} -2 \qquad -1$$

- Yes, the Bromine (Br) has been oxidized AND reduced (it is possible for both to happen to the same type of chemical species!).
- Now, we break the reaction into *two* half-reactions: the oxidation half-reaction and the reduction half-reaction.

Oxidation ¹ / ₂ Reaction:	$\operatorname{Br}_2 \operatorname{BrO}_3^-$
Reduction ½ Reaction:	$Br_2 \rightarrow Br^-$

• Next, we balance all the elements **EXCEPT FOR Hydrogen and Oxygen**:

Oxidation ¹ / ₂ Reaction:	$Br_2 \rightarrow 2BrO_3$
Reduction ¹ / ₂ Reaction:	$Br_2 \rightarrow 2Br^-$

• Now, to balance the **OXYGENS**, add water molecules to the half-reactions as needed:

Oxidation ½ Reaction: $Br_2 + 6H_2O \rightarrow 2BrO_3^-$ Reduction ½ Reaction: $Br_2 \rightarrow 2Br^-$

• Then, to balance the **HYDROGENS**, add protons (H⁺) to the half-reactions as needed:

Oxidation $\frac{1}{2}$ Reaction: $Br_2 + 6H_2O \rightarrow 2BrO_3^- + 12H^+$

Reduction $\frac{1}{2}$ Reaction: $Br_2 \rightarrow 2Br^-$

Next, we before we balance charge by adding electrons, we must recognize that it is not
possible to have protons floating around in a basic solution which has excess hydroxide
ions! So wherever we see protons, add the exact same amount of OH⁻ ions to both sides
of the equation (this keeps the half-reaction balanced, but takes care of the protons).

Oxidation ½ Reaction: $Br_2 + 6H_2O + 12OH^- \rightarrow 2BrO_3^- + 12H^+ + 12OH^-$ Reduction ½ Reaction: $Br_2 \rightarrow 2Br^-$

• Anytime a proton and a hydroxide are on the same side of a reaction, they combine to form a water molecule. We can reduce the amount of water molecules in a reaction

Oxidation ½ Reaction: $Br_2 + 6H_2O + 12OH^- \rightarrow 2BrO_3^- + 12H_2O$

Simplified Oxidation ½ Reaction: Br₂ + 12OH⁻ → 2BrO₃⁻ + 6H₂O

Reduction $\frac{1}{2}$ Reaction: $Br_2 \rightarrow 2Br^-$

• Now, balance **CHARGE** by adding electrons. Note that electrons are added to the products side in the oxidation half-reaction and to the reactants side in the reduction half-reaction. This should always be true:

Oxidation $\frac{1}{2}$ Reaction: $Br_2 + 12OH^- \rightarrow 2BrO_3^- + 6H_2O + 10e^-$

Reduction $\frac{1}{2}$ Reaction: $Br_2 + 2e^- \rightarrow 2Br^-$

- We would like to combine these two half-reactions into a final overall reaction. We must cancel out all the electrons because these are not part of our overall equation. Right now if we tried to add our equations, we would be in trouble! The number of electrons on the reactants side (2e) is less than the number of electrons on the products side (10e).
- So, we balance the half-reactions like an algebraic system of equations. Here, we will leave the oxidation half-reaction alone, but multiply everything in the reduction reaction by 5 in order to bring the total number of electrons up to 10 electrons:

Oxidation $\frac{1}{2}$ Reaction: Br₂ + 12OH⁻ \rightarrow 2BrO₃⁻ + 6H₂O + 10e⁻

Reduction $\frac{1}{2}$ Reaction: $5x(Br_2 + 2e^- \rightarrow 2Br^-)$

New Reduction $\frac{1}{2}$ Reaction: $5Br_2 + 10e^- \rightarrow 10Br^-$

• Combine the new half-reactions. Note that all of the electrons have cancelled out:

Oxidation $\frac{1}{2}$ Reaction: $Br_2 + 12OH^- \rightarrow 2BrO_3^- + 6H_2O + 10e^-$

<u>New Reduction $\frac{1}{2}$ Reaction: + $5Br_2 + 10e^- \rightarrow 10Br^-$ </u>

Overall Reaction: $Br_2 + 12OH^- + 5Br_2 \rightarrow 2BrO_3^- + 6H_2O + 10Br^-$

• Continue to balance the reaction by combining "like" terms and reducing the number of water molecules and protons:

Balanced Equation: $12OH^-+6Br_2 \rightarrow 2BrO_3^-+6H_2O+10Br^-$

• It is perfectly acceptable to have hydroxides in our final balanced equation because we are in a basic solution, which contains excess hydroxide.

Practice:

Balance the following reactions using the half-reaction method in a *basic* solution.

- 1. $NH_3 + ClO^- \rightarrow N_2H_2 + Cl^-$
- 2. $Fe + NiO_2 \rightarrow Fe(OH)_2 + Ni(OH)_2$
- 3. $MnO_4^- + CN^- \rightarrow MnO_2 + CNO^-$

Summary

- 1. Assign oxidation to all species.
- 2. Break reaction into to half-reactions: oxidation half-reaction and reduction half-reaction
- 3. Balance all species **EXCEPT HYDROGEN AND OXYGEN**.
- 4. Balance **OXYGEN** by adding water to the necessary sides of the half-reactions.
- 5. Balance **HYDROGEN** by adding protons (H⁺) to the necessary sides

5a. If in **ACIDIC SOLUTION** jump to step #6.

5b. If in **BASIC SOLUTION**, add the exact same amount of hydroxides (OH⁻) as there are protons to *both* sides of the half-reaction. Collapse protons and hydroxides that are on the same side of a half-reaction into water molecules and simplify the number of water across the half-reaction.

6. Balance **CHARGE** by adding electrons to the half-reactions. Remember to multiply the charges on a different species by the coefficients! Note that electrons are added to the products side in the oxidation half-reaction and to the reactants side in the reduction half-reaction. This should always be true.

- 7. Make the number of electrons in both half-reactions equal by multiplying by coefficients.
- 8. Combine the two half-reactions. Combine any "like" terms and simplify!