BALANCING REDOX EQUATIONS

The following steps may be used to balance oxidation–reduction (redox) equations by the ion–electron (half–reaction) method. While other methods may be successful, none is so consistently successful as is this particular method. The half–reactions used in this process will also be necessary when considering other electrochemical phenomena, thus the usefulness of half–reactions goes beyond balancing redox equations.

The basic idea of this method is to split a "complicated" equation into two parts called half–reactions. These simpler parts can be balanced separately, and then recombined to produce a balanced overall equation. The splitting is done so that one of the half–reactions only deals with the oxidation portion of the redox process, while the other only deals with the reduction portion. What ties the two halves together is the fact that the total electrons lost by the oxidation process MUST equal the total gained by the reduction process (step 7).

It is very important that you follow each of the steps listed below completely, and in order; do not try to take any short–cuts. There are many modifications of this method. For example there is a modification that allows you to balance all the reactions as if they were in acidic solution followed by a step, when necessary, to convert to a basic solution. Switching to a modification before you completely understand this method very often leads to confusion, and hence an incorrect result. The steps are:

1. CONVERT TO IONIC FORM

   (This is only necessary if the equation is not already in ionic form. If this step is done then step 9 must be done also.)

To do this all strong acids, strong bases, and soluble ionic compounds are separated into their individual ions. Molecular compounds (most materials containing only nonmetals that are neither acids, bases, nor polyatomic ions), insoluble ionic materials, gases, and weak acids and bases are not separated. (There are a few exceptions; these will be noted when necessary.)

Example:

CH₃OH + K₂Cr₂O₇ + H₂SO₄ → HCOOH + Cr₂(SO₄)₃ + K₂SO₄ + H₂O

Becomes:

CH₃OH + 2 K⁺ + Cr₂O₇²⁻ + 2 H⁺ + SO₄²⁻ → HCOOH + 2 Cr³⁺ + 3 SO₄²⁻ + 2 K⁺ + SO₄²⁻ + H₂O

Molecular:      CH₃OH, H₂O
Soluble Ionic:  K₂Cr₂O₇, Cr₂(SO₄)₃, K₂SO₄
Strong Acid:    H₂SO₄
Weak Acid:      HCOOH

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2. **Assign Oxidation Numbers and Begin the Half-Reactions, One for Oxidation and One for Reduction.**

(For many reactions, the substance oxidized, and the substance reduced will be obvious, so this step may be simplified. However, to be safe, at least do a partial check to confirm your predictions. Note: one substance may be both oxidized and reduced; do not let this situation surprise you—it is called disproportionation.)

Review the rules for assigning oxidation numbers if necessary. These numbers are only used in this step. Do not force them into step 6.

Start the half–reactions with the entire molecules or ions from the net ionic form of the reaction. Do not go back to the molecular form of the reaction or just pull out atoms from their respective molecules or ions. Thus from the example above, the initial half–reactions should be:

\[ \text{CH}_3\text{OH} \rightarrow \text{HCOOH} \]
\[ \text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+} \]

The carbon is oxidized (C\(^2-\) to C\(^2+\)) and the chromium is reduced (Cr\(^{6+}\) to Cr\(^{3+}\)). Check to make sure you get the same oxidation numbers for the carbon and the chromium (hydrogen and oxygen are +1 and −2 respectively).

3. **Balance All Atoms Except Oxygen and Hydrogen.**

(In many reactions this will have been done in step 2; because of this many people forget to check this step. This is a very common reason why people get the wrong result.)

In the above example carbon (C) and chromium (Cr) are the elements to be considered. The carbon is balanced, so no change is required in the first half–reaction. The chromium needs to be balanced, and so the second half–reaction becomes:

\[ \text{Cr}_2\text{O}_7^{2-} \rightarrow 2 \text{Cr}^{3+} \]

**NOTE:**

To carry out the next two steps correctly, it is necessary to know if the solution is acidic or basic. A basic solution is one in which you are specifically told is basic, or one that contains a base of OH\(^-\) anywhere within the reaction. Assume that all other solutions are acidic (even if no acid is present).
4. **BALANCE OXYGEN ATOMS**
   a. **IN ACIDIC SOLUTIONS** ADD 1 H₂O/O TO THE SIDE NEEDING OXYGEN
   b. **IN BASIC SOLUTIONS** ADD 2 OH⁻ FOR EVERY OXYGEN NEEDED ON THE OXYGEN DEFICIENT SIDE PLUS 1 H₂O/O ON THE OPPOSITE SIDE.

Do not forget that two things (OH⁻ and H₂O) must be added in a basic solution. Also these must be added to opposite sides.

Examples:

Acid: \( \text{Cr}_2\text{O}_7^{2-} \rightarrow 2 \text{Cr}^{3+} \)
becomes:
\( \text{Cr}_2\text{O}_7^{2-} \rightarrow 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O} \)

Base: \( \text{Cr}_2\text{O}_7^{2-} \rightarrow 2 \text{CrO}_2^- \)
becomes:
\( 3 \text{H}_2\text{O} + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2 \text{CrO}_2^- + 6 \text{OH}^- \)

5. **BALANCE HYDROGEN ATOMS**
   a. **IN ACIDIC SOLUTIONS** ADD H⁺(aq)
   b. **IN BASIC SOLUTIONS** ADD 1 H₂O/H NEEDED PLUS 1 OH⁻/H ON THE OPPOSITE SIDE.

Again, do not forget that two things must be added in basic solutions (OH⁻ and H₂O). In this case they are still added to opposite sides, but with a different ratio.

Examples:

Acid: \( \text{Cr}_2\text{O}_7^{2-} \rightarrow 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O} \)
becomes:
\( 14 \text{H}^+(aq) + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O} \)

Base: \( 6 \text{OH}^- + \text{C}_2\text{H}_5\text{OH} \rightarrow 2 \text{CO}_2 + 3 \text{H}_2\text{O} \)
becomes:
\( 6 \text{OH}^- + 6 \text{OH}^- + \text{C}_2\text{H}_5\text{OH} \rightarrow 2 \text{CO}_2 + 3 \text{H}_2\text{O} + 6 \text{H}_2\text{O} \)

If the basic step is done correctly, the oxygen atoms should remain balanced. This may be used as a check at this point.
6. **BALANCE CHARGES BY ADDING ELECTRONS.**

The electrons must appear on opposite sides of the two half–reactions. They will appear on the left for the reduction, and on the right for the oxidation. Once added make sure you check and make sure that the total charge on each side is the same. Not being careful on this step is a major cause of incorrect answers. Do not forget to use both the coefficients and the overall charges on the ionic species (not the oxidation numbers from step 2).

Examples:

**Acid:**

\[6 \text{ e}^- + 14 \text{ H}^+(aq) + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2 \text{ Cr}^{3+} + 7 \text{ H}_2\text{O}\]

**Base:**

\[6 \text{ OH}^- + 6 \text{ OH}^- + \text{C}_2\text{H}_5\text{OH} \rightarrow 2 \text{ CO}_2 + 3 \text{ H}_2\text{O} + 6 \text{ H}_2\text{O} + 12 \text{ e}^-\]

7. **ADJUST THE HALF–REACTIONS SO THAT THEY BOTH HAVE THE SAME NUMBER OF ELECTRONS.**

(Find the lowest common multiple, and multiply each of the half–reactions by the appropriate factor to achieve this value. This is the key step as the number of electrons lost MUST equal the number gained.)

Example:

Lowest common multiple = 12

\[3 \times (\text{H}_2\text{O} + \text{CH}_3\text{OH} \rightarrow \text{HCOOH} + 4 \text{ H}^+(aq) + 4 \text{ e}^-)\]
\[2 \times (6 \text{ e}^- + 14 \text{ H}^+(aq) + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2 \text{ Cr}^{3+} + 7 \text{ H}_2\text{O})\]

Giving:

\[3 \text{ H}_2\text{O} + 3 \text{ CH}_3\text{OH} \rightarrow 3 \text{ HCOOH} + 12 \text{ H}^+(aq) + 12 \text{ e}^-\]
\[12 \text{ e}^- + 28 \text{ H}^+(aq) + 2 \text{ Cr}_2\text{O}_7^{2-} \rightarrow 4 \text{ Cr}^{3+} + 14 \text{ H}_2\text{O}\]

8. **ADD THE HALF–REACTIONS AND CANCEL.**  

(The electrons must cancel)

Example (from step 7):

\[12 \text{ e}^- + 3 \text{ H}_2\text{O} + 3 \text{ CH}_3\text{OH} + 28 \text{ H}^+(aq) + 2 \text{ Cr}_2\text{O}_7^{2-} \rightarrow\]

\[4 \text{ Cr}^{3+} + 14 \text{ H}_2\text{O} + 3 \text{ HCOOH} + 12 \text{ H}^+(aq) + 12 \text{ e}^-\]

Becomes:

\[3 \text{ CH}_3\text{OH} + 16 \text{ H}^+(aq) + 2 \text{ Cr}_2\text{O}_7^{2-} \rightarrow 4 \text{ Cr}^{3+} + 11 \text{ H}_2\text{O} + 3 \text{ HCOOH}\]
9. **CONVERT THE EQUATION BACK TO MOLECULAR FORM.**

(This step is only necessary if the equation was originally in molecular form, and converted to ionic form in step 1. Otherwise skip to step 10.)

Example (using steps 1 and 8):

\[ 3 \text{CH}_3\text{OH} + 16 \text{H}^+ (aq) + 2 \text{Cr}_2\text{O}_7^{2-} \rightarrow 4 \text{Cr}^{3+} + 11 \text{H}_2\text{O} + 3 \text{HCOOH} \]

Needs: \[ + 8 \text{SO}_4^{2-} + 4 \text{K}^+ + 8 \text{SO}_4^{2-} + 4 \text{K}^+ \]

Giving:

\[ 3 \text{CH}_3\text{OH} + 8 \text{H}_2\text{SO}_4 + 2 \text{K}_2\text{Cr}_2\text{O}_7 \rightarrow 2 \text{Cr}_2(\text{SO}_4)_3 + 11 \text{H}_2\text{O} + 3 \text{HCOOH} + 2 \text{K}_2\text{SO}_4 \]

10. **CHECK TO SEE IF ALL ATOMS BALANCE AND THAT THE TOTAL CHARGE ON EACH SIDE IS THE SAME.**

This step will let you know if you have done everything correctly.

If all the atoms and charges do not balance you have made a mistake. Look over your work. If you have made an obvious mistake, then you should correct it. If the mistake is not obvious, it may take less time to start over from the beginning. The most common mistakes are made in steps 3 and 6, or step 4 in a basic solution.

Make sure you learn to apply each of the above steps. Look over the individual examples and make sure you understand them separately. Then make sure you learn the order of these steps. Finally, balance redox reactions, this will take a lot of practice. Make sure that you reach the point of being able to consistently balance equations without looking at the rules.
Balancing Oxidation–Reduction Equations

Determine oxidation states as indicated:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Element</th>
<th>Oxidation state</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. K₂CrO₄</td>
<td>Cr</td>
<td>__________</td>
</tr>
<tr>
<td>2. KMnO₄</td>
<td>Mn</td>
<td>__________</td>
</tr>
<tr>
<td>3. KIO₃</td>
<td>I</td>
<td>__________</td>
</tr>
<tr>
<td>4. NaAsO₃</td>
<td>As</td>
<td>__________</td>
</tr>
<tr>
<td>5. FeCl₃</td>
<td>Fe</td>
<td>__________</td>
</tr>
</tbody>
</table>

Balance the following half–reactions by ion–electron method:

1. \( \text{MnO}_4^- \rightarrow \text{Mn}^{2+} \) (acid)

2. \( \text{IO}_3^- \rightarrow \text{I}_2 \) (acid)

3. \( \text{BrO}_3^- \rightarrow \text{Br}_2 \) (basic)

4. \( \text{Cl}_2 \rightarrow \text{ClO}_5^- \) (basic)
Balance the following reactions: (Assume all reactions are in the presence of water.)

1. \( S^{2-} + Cr_2O_7^{2-} + H^+ \rightarrow S + Cr^{3+} + H_2O \)
2. \( Cl_2 + H_2O + SO_2 \rightarrow SO_4^{2-} + Cl^- + H^+ \)
3. \( Mn^{2+} + PbO_2 + H^+ \rightarrow MnO_4^- + Pb^{2+} + H_2O \)
4. \( SnO_2^{2-} + Bi^{3+} + OH^- \rightarrow SnO_3^{2-} + Bi + H_2O \)
5. \( ClO_2^- + MnO_4^- \rightarrow MnO_2 + ClO_4^- \) (basic)
6. \( Cr_2O_7^{2-} + HAsO_2 + H^+ \rightarrow H_3AsO_4 + Cr^{3+} + H_2O \)
7. \( S_2O_3^{2-} + I_2 + OH^- \rightarrow SO_4^{2-} + I^- + H_2O \)
8. \( BrO_4^- + Zn + OH^- + H_2O \rightarrow Br^- + [Zn(OH)_4]^{2-} \)
9. \( S^{2-} + NO_3^- \rightarrow S + NO_2 \) (acidic)
10. \( NO_2 + OH^- \rightarrow NO_2^- + NO_3^- + H_2O \)
11. \( Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO + H_2O \)
12. \( K_2CrO_4 + H_2S + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + S + H_2O \)
13. \( FeCl_2 + K_2Cr_2O_7 + HCl \rightarrow FeCl_3 + KCl + CrCl_3 + H_2O \)
14. \( P_4 + KOH + H_2O \rightarrow K_2HPO_3 + PH_3 \)
15. \( KBrO_3 + KBr + H_2SO_4 \rightarrow K_2SO_4 + Br_2 + H_2O \)
16. \( NaNO_3 + Zn + H_2O \rightarrow NaOH + Zn(OH)_2 + NH_3 \)
17. \( K_2Cr_2O_7 + KI + HCl \rightarrow CrCl_3 + I_2 + KCl + H_2O \)
18. \( NaCrO_2 + Na_2O_2 + H_2O \rightarrow NaOH + Na_2CrO_4 \)
19. \( H_2SO_3 + I_2 + H_2O \rightarrow H_2SO_4 + HI \)
20. \( Li_2SeO_3 + PbO_2 + H_2O \rightarrow Li_2SeO_4 + Pb(OH)_2 \)
21. \( Br_2 + KOH \rightarrow KBrO_3 + KBr + H_2O \)
22. \( CH_3CH_2OH + KMnO_4 + HCl \rightarrow CH_3COOH + MnCl_2 + KCl + H_2O \)
23. \( Cr_2(SO_4)_3 + (NH_4)_2S_2O_8 + H_2O \rightarrow H_2CrO_4 + (NH_4)_2SO_4 + H_2SO_4 \)
24. \( CH_3OH + KMnO_4 \rightarrow HCOOK + MnO_2 + KOH + H_2O \)

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