Balancing redox reactions in basic solution

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Points to remember:

1) Electrons NEVER appear in a correct, final answer. In order to get the electrons in each half-reaction equal, one or both of the balanced half-reactions will be multiplied by a factor.

2) Duplicate items are always removed. These items are usually the electrons, water and hydroxide ion.

Example #1: $NH_3 + ClO^- \text{--->} N_2H_4 + Cl^-$

Solution:

1) The two half-reactions, balanced as if in acidic solution:

$2NH_3 \text{--->} N_2H_4 + 2H^+ + 2e^-$
$2e^- + 2H^+ + ClO^- \text{--->} Cl^- + H_2O$

2) Electrons already equal, convert to basic solution:

$2OH^- + 2NH_3 \text{--->} N_2H_4 + 2H_2O + 2e^-$
$2e^- + 2H_2O + ClO^- \text{--->} Cl^- + H_2O + 2OH^-$

Comment: that's 2 OH^-, not 20 H^-. Misreading the O in OH as a zero is a common mistake.

3) The final answer:

$2HN_3 + ClO^- \text{--->} N_2H_4 + Cl^- + H_2O$

Notice that no hydroxide appears in the final answer. That means this is a base-catalyzed reaction. For the reaction to occur, the solution must be basic and hydroxide IS consumed. It is just regenerated in the exact same amount, so it cancels out in the final answer.

Example #2: $Au + O_2 + CN^- \text{--->} Au(CN)_2^- + H_2O_2$

Solution:

1) the two half-reactions, balanced as if in acidic solution:

$2CN^- + Au \text{--->} Au(CN)_2^- + e^-$
$2e^- + 2H^+ + O_2 \text{--->} H_2O_2$

2) Make electrons equal, convert to basic solution:

$4CN^- + 2Au \text{ ---> } 2Au(CN)_2^- + 2e^-$ <--- multiplied by a factor of 2
$2e^- + 2H_2O + O_2 \text{ ---> } H_2O_2 + 2OH^-$

3) The final answer:

$4CN^- + 2Au + 2H_2O + O_2 \text{ ---> } 2Au(CN)_2^- + H_2O_2 + 2OH^-$

Comment: the CN^- is neither reduced nor oxidized, but it is necessary for the reaction. For example, you might see this way of writing the problem:

$Au + O_2 \text{ ---> } Au(CN)_2^- + H_2O_2$

Notice that CN^- does not appear on the left side, but does so on the right. Since you MUST balance the equation, that means you are allowed to use CN^- in your balancing. An important point here is that you know the cyanide polyatomic ion has a negative one charge.

Example #3: $Br^- + MnO_4^- \text{ ---> } MnO_2 + BrO_3^-$

Solution:

1) The two half-reactions, balanced as if in acidic solution:

$3H_2O + Br^- \text{ ---> } BrO_3^- + 6H^+ + 6e^-$
$3e^- + 4H^+ + MnO_4^- \text{ ---> } MnO_2 + 2H_2O$

2) Make the number of electrons equal:

$3H_2O + Br^- \text{ ---> } BrO_3^- + 6H^+ + 6e^-$
$6e^- + 8H^+ + 2MnO_4^- \text{ ---> } 2MnO_2 + 4H_2O$ <--- multiplied by a factor of 2

3) Convert to basic solution, by adding $6OH^-$ to the first half-reaction and $8OH^-$ to the second:

$6OH^- + Br^- \text{ ---> } BrO_3^- + 3H_2O + 6e^-$
$6e^- + 4H_2O + 2MnO_4^- \text{ ---> } 2MnO_2 + 8OH^-$

4) The final answer:

$H_2O + 2MnO_4^- + Br^- \text{ ---> } 2MnO_2 + BrO_3^- + 2OH^-$

5) What happens if you add the two half-reactions without converting them to basic?

You get this:

$2H^+ + 2MnO_4^- + Br^- \text{ ---> } 2MnO_2 + BrO_3^- + H_2O$

Then, add $2OH^-$ to each side:

$2H_2O + 2MnO_4^- + Br^- \text{ ---> } 2MnO_2 + BrO_3^- + H_2O + 2OH^-$

Eliminate one water for the final answer:

$H_2O + 2MnO_4^{-} + Br^{-} \text{--->} 2MnO_2 + BrO_3^{-} + 2OH^{-}$

The answer to the question? Nothing happens. You get the right answer if convert before adding the half-reactions or after. There will even be cases where balancing one half-reaction using hydroxide can easily be done while the other half-reaction gets balanced in acidic solution before converting. You can add the two half-reactions while one is basic and one is acidic, then convert after the adding (see below for an example of this).

Example #4: $AlH_4^{-} + H_2CO \text{--->} Al^{3+} + CH_3OH$

Solution:

1) The two half-reactions, balanced as if in acidic solution:

$AlH_4^{-} \text{--->} Al^{3+} + 4H^{+} + 8e^{-}$
$2e^{-} + 2H^{+} + H_2CO \text{--->} CH_3OH$

2) Converted to basic by addition of hydroxide, second half-reaction multiplied by 4 (note that the hydrogen is oxidized from -1 to +1):

$4OH^{-} + AlH_4^{-} \text{--->} Al^{3+} + 4H_2O + 8e^{-}$
$8e^{-} + 8H_2O + 4H_2CO \text{--->} 4CH_3OH + 8OH^{-}$

3) The final answer:

$AlH_4^{-} + 4H_2O + 4H_2CO \text{--->} Al^{3+} + 4CH_3OH + 4OH^{-}$

Example #5: $Se + Cr(OH)_3 \text{--->} Cr + SeO_3^{2-}$

Solution:

1) The unbalanced half-reactions:

$Se \text{--->} SeO_3^{2-}$
$Cr(OH)_3 \text{--->} Cr$

2) Note that only the first half-reaction is balanced using the balance-first-in-acid technique, the second is balanced using hydroxide:

$Se + 3H_2O \text{--->} SeO_3^{2-} + 6H^{+} + 4e^{-}$
$3e^{-} + Cr(OH)_3 \text{--->} Cr + 3OH^{-}$

3) Convert the first half-reaction by adding 6 hydroxide to each side, eliminate duplicate waters, then make the electrons equal (factor of 3 for the first half-reaction and a factor of 4 for the second). The final answer:

$6OH^{-} + 3Se + 4Cr(OH)_3 \text{--->} 4Cr + 3SeO_3^{2-} + 9H_2O$

4) What would happen if we didn't make the first half-reaction basic and just added them?

first, make the electrons equal:

$3Se + 9H_2O$ ---> $3SeO_3^{2-} + 18H^+ + 12e^-$
$12e^- + 4Cr(OH)_3$ ---> $4Cr + 12OH^-$

then, add:

$3Se + 4Cr(OH)_3 + 9H_2O$ ---> $4Cr + 3SeO_3^{2-} + 18H^+ + 12OH^-$

combine hydrogen ion and hydroxide ion on the right-hand side:

$3Se + 4Cr(OH)_3 + 9H_2O$ ---> $4Cr + 3SeO_3^{2-} + 6H^+ + 12H_2O$

eliminate water:

$3Se + 4Cr(OH)_3$ ---> $4Cr + 3SeO_3^{2-} + 6H^+ + 3H_2O$

add six hydroxides:

$6OH^- + 3Se + 4Cr(OH)_3$ ---> $4Cr + 3SeO_3^{2-} + 9H_2O$

Note that I combined the H^+ and the OH^- to make six waters and then added it to the three waters that were already there.