Balancing redox reactions in acidic 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 hydrogen ion.

Example #1: $ClO_3^- + SO_2 \text{ ---> } SO_4^{2-} + Cl^-$

Solution:

1) Split into unbalanced half-reactions:

$ClO_3^- \text{ ---> } Cl^-$
$SO_2 \text{ ---> } SO_4^{2-}$

2) Balance the half-reactions:

$6e^- + 6H^+ + ClO_3^- \text{ ---> } Cl^- + 3H_2O$
$2H_2O + SO_2 \text{ ---> } SO_4^{2-} + 4H^+ + 2e^-$

3) Make the number of electrons equal:

$6e^- + 6H^+ + ClO_3^- \text{ ---> } Cl^- + 3H_2O$
$6H_2O + 3SO_2 \text{ ---> } 3SO_4^{2-} + 12H^+ + 6e^-$ <--- multiplied through by a factor of 3

4) Add the two half-reactions for the final answer:

$ClO_3^- + 3H_2O + 3SO_2 \text{ ---> } 3SO_4^{2-} + Cl^- + 6H^+$

Note that items duplicated on each side were cancelled out. The duplicates are $6e^-$, $3H_2O$, and $6H^+$

Example #2: $H_2S + NO_3^- \text{ ---> } S_8 + NO$

Solution:

1) The unbalanced half-reactions:

H_2S ---> S_8
NO_3^- ---> NO

2) balance each half-reaction:

$8H_2S$ ---> $S_8 + 16H^+ + 16e^-$
$3e^- + 4H^+ + NO_3^-$ ---> $NO + 2H_2O$

3) Make the number of electrons equal:

$24H_2S$ ---> $3S_8 + 48H^+ + 48e^-$ <--- multiplied by a factor of 3
$48e^- + 64H^+ + 16NO_3^-$ ---> $16NO + 32H_2O$ <--- multiplied by a factor of 16

Note that 16 and 3 have no common factors except 1, so both 16 and 3 had to be used to obtain the lowest common multiple of 48 for the number of electrons.

4) Add:

$24H_2S + 16H^+ + 16NO_3^-$ ---> $3S_8 + 16NO + 32H_2O$

Comment: removing a factor of 8 does look tempting, doesn't it? However, the three in front of the S_8 (or the five in the next problem) makes it impossible. Also, note that duplicates of 48 electrons and 48 hydrogen ions were removed.

Example #3: $MnO_4^- + H_2S$ ---> $Mn^{2+} + S_8$

Solution:

1) Half-reactions:

H_2S ---> S_8
MnO_4^- ---> Mn^{2+}

2) Balance:

$8H_2S$ ---> $S_8 + 16H^+ + 16e^-$
$5e^- + 8H^+ + MnO_4^-$ ---> $Mn^{2+} + 4H_2O$

3) Make the number of electrons equal (note that there are no common factors between 5 and 16 except 1):

$40H_2S$ ---> $5S_8 + 80H^+ + 80e^-$ <--- factor of 5
$80e^- + 128H^+ + 16MnO_4^-$ ---> $16Mn^{2+} + 64H_2O$ <--- factor of 16

4) The final answer:

$40H_2S + 48H^+ + 16MnO_4^-$ ---> $5S_8 + 16Mn^{2+} + 64H_2O$

Another possibility of removing a factor of 8 destroyed by an odd number, in this case, the 5 in front of the S_8. Curses, foiled again!

Example #4: $Cu + SO_4^{2-}$ ---> $Cu^{2+} + SO_2$

1) The unbalanced half-reactions:

Cu ---> Cu^{2+}
SO_4^{2-} ---> SO_2

2) The balanced half-reactions:

Cu ---> $Cu^{2+} + 2e^-$
$2e^- + 4H^+ + SO_4^{2-}$ ---> $SO_2 + 2H_2O$

3) The final answer:

$Cu + 4H^+ + SO_4^{2-}$ ---> $Cu^{2+} + SO_2 + 2H_2O$

No need to equalize electrons since it turns out that, in the course of balancing the half-reactions, the electrons are equal in amount. Note how easy it was to balance the copper half-reaction. All you needed were the two electrons.

Example #5: $MnO_4^- + CH_3OH$ ---> $HCOOH + Mn^{2+}$

1) The balanced half-reactions:

$5e^- + 8H^+ + MnO_4^-$ ---> $Mn^{2+} + 4H_2O$
$H_2O + CH_3OH$ ---> $HCOOH + 4H^+ + 4e^-$

2) Equalize electrons:

$20e^- + 32H^+ + 4MnO_4^-$ ---> $4Mn^{2+} + 16H_2O$ <--- factor of 4
$5H_2O + 5CH_3OH$ ---> $5HCOOH + 20H^+ + 20e^-$ <--- factor of 5

3) The final answer:

$12H^+ + 5CH_3OH + 4MnO_4^-$ ---> $5HCOOH + 4Mn^{2+} + 11H_2O$

Bonus Example: $Cr_2O_7^{2-} + SO_2 + H^+$ ---> $Cr^{3+} + HSO_4^- + H_2O$

Solution:

1) Half-reactions:

$Cr_2O_7^{2-}$ ---> Cr^{3+}
SO_2 ---> HSO_4^-

2) Balance in acidic solution:

$6e^- + 14H^+ + Cr_2O_7^{2-} \text{--->} 2Cr^{3+} + 7H_2O$

$2H_2O + SO_2 \text{--->} HSO_4^- + 3H^+ + 2e^-$

3) Equalize electrons:

$6e^- + 14H^+ + Cr_2O_7^{2-} \text{--->} 2Cr^{3+} + 7H_2O$

$6H_2O + 3SO_2 \text{--->} 3HSO_4^- + 9H^+ + 6e^-$

4) Add:

$5H^+ + Cr_2O_7^{2-} + 3SO_2 \text{--->} 2Cr^{3+} + 3HSO_4^- + H_2O$

Sometimes you are given a net-ionic equation and asked to take it back to a full molecular equation. Sometimes, no context is added, so you have to make some informed predictions. Here's what I mean:

Since the equation is in acidic solution, you can use HCl or HNO_3. I'll use HCl. The most common dichromate that is soluble is potassium dichromate, so we will use that. Using those, we find this:

$5HCl + K_2Cr_2O_7 + 3SO_2 \text{--->} 2CrCl_3 + 3KHSO_4 + H_2O$

However, there is a problem. One too many K and Cl on the right-hand side. The solution is to add one KCl to the left-hand side:

$KCl + 5HCl + K_2Cr_2O_7 + 3SO_2 \text{--->} 2CrCl_3 + 3KHSO_4 + H_2O$

You can write the equation using HNO_3 and the nitrate would simply replace the chloride.

Using sulfuric acid can be done but (and this is part of the informed prediction) probably should not. The chromium(III) ion is presented as an ion, meaning it's soluble. Chromium(III) sulfate is not soluble, which means you would have to write the full formula. Since that was not done, we conclude that the chromium ion was part of a soluble compound. This whole balance-a-redox-reaction-in-molecular-form is a thing and it's not covered very much in most textbooks. Here are some examples.