REDOX REACTIONS

At the end of this chapter, you should be able to:

- Explain redox reactions in terms of electron transfer and changes in oxidation state (number).
- Deduce balanced equations for redox reactions from relevant half equations;
- Perform simple displacement reactions to order elements in terms of oxidizing or reducing ability.

4.1. THE CONCEPT OF REDOX

Redox reactions, or oxidation-reduction reactions, have a number of similarities to acid-base reactions. Fundamentally, redox reactions are a family of reactions that are concerned with the transfer of electrons between species. Like acid-base reactions, redox reactions are a matched set - you don't have an oxidation reaction without a reduction reaction happening at the same time.

Oxidation refers to the loss of electrons, while reduction refers to the gain of electrons. Each reaction by itself is called a **half – reaction**, simply because we need two (2) half-reactions to form a whole reaction. In notating redox reactions, chemists typically write out the electrons explicitly:

$$\mathrm{Cu\ (s)} \rightarrow \mathrm{Cu^{2+}} + 2\ \mathrm{e^-}$$

This half – reaction says that we have solid copper (with no charge) being oxidized (losing electrons) to form a copper ion with a plus 2 charge. Notice that, like the stoichiometry notation, we have a **balance** between both sides of the reaction. We have one (1) copper atom on both sides, and the charges balance as well. The symbol e^- represents a free electron with a negative charge that can now go out and reduce some other species, such as in the half-reaction:

$$2\ \mathrm{Ag}^+\ (\mathrm{aq}) +\ 2\ \mathrm{e}^- \rightarrow\ 2\ \mathrm{Ag}\ (\mathrm{s})$$

Here, two silver ions (silver with a positive charge) are being reduced through the addition of two (2) electrons to form solid silver. The abbreviations aq and s mean aqueous and solid, respectively. We can now combine the two (2) half-reactions to form a redox equation:

$$\mathrm{Cu}\ (\mathrm{s}) \rightarrow\ \mathrm{Cu}^{2+}\ +\ 2\ \mathrm{e}^-$$
$$2\ \mathrm{Ag}^+\ (\mathrm{aq}) +\ 2\ \mathrm{e}^- \rightarrow\ 2\ \mathrm{Ag}\ (\mathrm{s})$$

Adding gives:

$$\mathrm{Cu(s)} + 2\mathrm{Ag}^+(\mathrm{aq}) + 2\mathrm{e}^- \rightarrow 2\mathrm{Ag(s)} + \mathrm{Cu}^{2+} + 2\mathrm{e}^-$$

Since the $2e^-$ are found on both sides of the equation, they can cancel.

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

We can also discuss the individual components of these reactions as follows. If a chemical causes another substance to be oxidized, we call it the **oxidizing agent**. In the equation above, Ag^+ is the oxidizing agent, because it causes Cu(s) to lose electrons. Oxidants get reduced in the process by a **reducing agent**. Cu(s) is, naturally, the reducing agent in this case, as it causes Ag^+ to gain electrons.

4.2. OXIDATION NUMBER

In considering redox reactions, you must have some sense of the oxidation number (ON) of the compound. The **oxidation number** is defined as the effective charge on an atom in a compound, calculated according to a prescribed set of rules. An increase in oxidation number corresponds to oxidation, and a decrease to reduction. The oxidation number of a compound has some analogy to the pH and pK measurements found in acids and bases – the oxidation number suggests the strength or tendency of the compound to be oxidized or reduced, to serve as an oxidizing agent or reducing agent. The rules are shown below. Go through them in the order given until you have an oxidation number assigned.

1. For atoms in their elemental form, the oxidation number is 0

2. For ions, the oxidation number is equal to their charge

3. For single hydrogen, the number is usually +1 but in some cases it is -1

4. For oxygen, the number is usually -2

5. The sum of the oxidation number (ONs) of all the atoms in the molecule or ion is equal to its total charge.

As a side note, the term **oxidation**, with its obvious root from the word **oxygen**, assumes that oxygen has an oxidation number of -2. Using this as a benchmark, oxidation numbers were assigned to all other elements. For example, if we look at H_2O, and assign the value of -2 to the oxygen atom, the hydrogens must each have an oxidation number of +1 by default, since water is a neutral molecule.

Example

As an example, what is the oxidation number of sulphur in sulphur dioxide (SO_2)?

Solution

Given that each oxygen atom has a -2 charge, and knowing that the molecule is neutral, the oxidation number for sulphur must be +4.

Problem

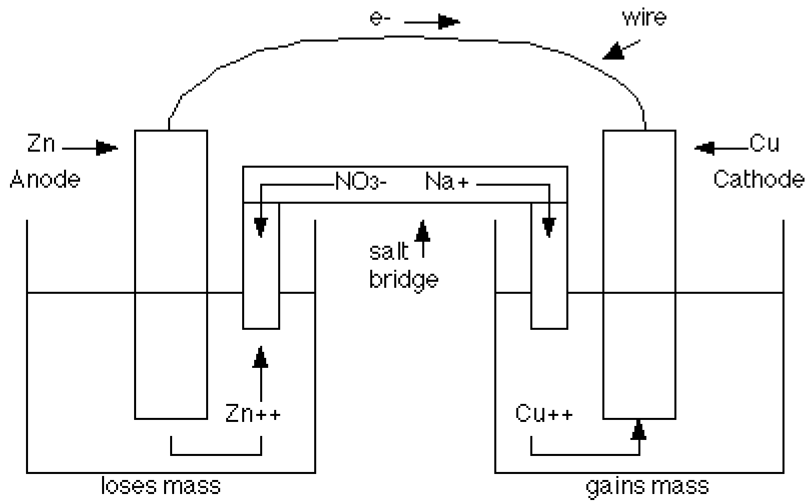
What about for a sulfate ion (SO_4^{2-})?

Solution

Again, the charge of all the oxygen atoms is 4 x -2 = -8. Sulphur must then have an oxidation number of +6, since +6 + (-8) = -2, the total charge on the ion. Since the sulphur in sulphate has a higher oxidation number than in sulphur dioxide, it is said to be more highly oxidized.

The energy released in any spontaneous redox reaction can be used to perform electrical work using an **electrochemical cell** (a device where electron transfer is forced to take an external pathway instead of going directly between the reactants. Think of the reaction between zinc and copper. Instead of placing a piece of zinc directly into a solution containing copper, we can form a cell where solid pieces of zinc and copper are placed in two different solutions such as sodium nitrate. The two solids are called electrodes. The *anode* is the electrode where oxidation occurs and mass is lost where as the cathode is the electrode where reduction occurs and mass is gained. The two electrodes are connected by a circuit and the two (2) solutions are connected by a "salt bridge" which allows ions to pass through. The anions are the negative ions and they move towards the anode. The cations are the positive ions and they move towards the cathode.

The following is a diagram of an electrochemical cell with zinc and copper acting as the electrodes.



An electrochemical cell of the reaction:
Zn(s) + Cu++(aq) → Zn++(aq) + Cu(s)

An external electric current hooked up to an electrochemical cell will make the electrons go backwards. This process is called electrolysis. This is used, for example, to make something gold plated. You would put the copper in a solution with gold and add a current which causes the gold ions to bond to the copper and therefore coating the copper. The time, current, and electrons needed determine how much "coating" occurs. The key to solving electrolysis problems is learning how to convert between the units. Useful information: 1 A=1 C/sec; 96,500 coulombs can produce one (1) mole of e^-; the electrons needed is determined by the charge of the ion involved

4.3. BALANCING REDOX REACTIONS IN ACID SOLUTION

Balancing redox reactions in acid can be easy, if you follow the rules. We'll work through an example step by step introducing each rule in turn.

Suppose you want to balance the following equation:

$$Cr_2O_7^{2-} + NO_2^- \rightarrow Cr^{3+} + NO_3^- \text{ (acid)}$$

First, split the reaction into two half reactions. One of the half reactions will show the oxidation; the other half reaction will show the reduction. It is not necessary at this point to know in advance which is which:

$$Cr_2O_7^{2-} \rightarrow Cr^{3+}$$

$$NO_2^- \rightarrow NO_3^-$$

Balance any atom other than oxygen or hydrogen first. Work with one half reaction at a time. In the first half reaction, there are 2 Cr on the left hand side and only 1 Cr on the right hand side. Balance the Cr first:

$$Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$$

Next, balance the O by adding as much H_2O as needed to the side deficient in O. In this case, 7 H_2O is needed on the right hand side to balance the 7 O on the left hand side:

$$Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$$

Since this reaction occurs in acid solution, balance the H by using H^+ ions. Add as many H^+ ions as needed to the side deficient in H. In this case, 14 H^+ ions are needed on the left hand side of the half reaction:

$$14\,H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$$

Mass balance has now been achieved for this half reaction.

All that remains is charge balance. To balance the charge, find the net charge on each side of the half reaction, and add as many electrons as needed to the more positive side so as to equal the charge on the more negative side.

In this case the net charge on the left hand side of the half reaction is +12 (+14 for the 14 hydrogen ions and -2 for the dichromate ion).

The net charge on the right hand side is +6 (+6 due to two Cr^{3+} ions and 0 for the 7 water molecules).

The net charge on the left hand side (+12) is more positive than the charge on the right hand side (+6). By adding 6 electrons (6e-) to the left hand side, the net charge will be the same on both sides of the half reaction:

$$6\,e^{-} + \; 14\,H^{+} + \; Cr_2O_7^{2-} \rightarrow \; 2Cr^{3+} + \; 7H_2O$$

This half reaction is now mass and charge balanced, and shows the reduction. Notice how electrons are on the reactant side which means they are being gained (reduction involves gaining electrons).

Repeat the same steps for the second half reaction:

$$\mathrm{NO_2^-} \rightarrow \; \mathrm{NO_3^-}$$

Balance the oxygen by using water. Add 1 H_2O to the left hand side of the half reaction:

$$\mathrm{H_2O} \; + \; \mathrm{NO_2^-} \rightarrow \; \mathrm{NO_3^-}$$

Balance the hydrogens by adding H^+ to the side deficient in H. In this case, add 2 H^+ to the right hand side of the half reaction:

$$\mathrm{H_2O} \; + \; \mathrm{NO_2^-} \rightarrow \; \mathrm{NO_3^-} \; + \; \mathrm{2H^+}$$

Mass balance has now been achieved. To balance the charge, add electrons to the more positive side to equal the less positive side of the half reaction. In this case, the net charge on the left hand side of the half reaction is -1; the net charge on the right hand side of the half reaction is +1. The right hand sides of the half reaction is more positive, so add 2 electrons to the right hand side to make the net charge on both sides of the half reaction -1:

$$H_2O + NO_2^- \rightarrow NO_3^- + 2H^+ + 2e^-$$

This half reaction is now both mass and charge balanced, and shows the oxidation. Notice how electrons are on the product side of the half reaction which means they are being lost (oxidation is a loss of electrons).

Before you can add up the two half reactions to the balanced net ionic reaction, the number of electrons lost must equal the number of electrons gained. Examination of the two half reactions shows 2 electrons lost and 6 electrons gained:

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

$$H_2O + NO_2^- \rightarrow NO_3^- + 2\,H^+ + 2\,e^-$$

You need to find the least common multiple (lcm) of 2 and 6. In this case, the lcm is 6. Next, multiply each of the half reactions by the factor needed to obtain the 1 cm. Therefore, multiply the first half reaction by 1 and the second half reaction by 3:

$$1 \times (6\,e^- + 14\,H^+ + Cr_2O_7^{2-} \rightarrow 2\,Cr^{3+} + 7\,H_2O)$$

$$3 \times (H_2O + NO_2^- \rightarrow NO_3^- + 2\,H^+ + 2\,e^-)$$

This yields the following half reactions:

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

$$3\,H_2O + 3\,NO_2^- \rightarrow 3\,NO_3^- + 6\,H^+ + 6\,e^-$$

Next, cancel any terms which are common to both sides of the half reactions. For instance, the 6 electrons may be cancelled, the 3 H_2O on the left hand side of the second half reaction will cancel 3 of the 7 H_2O on the right hand side of the first half reaction, and the 6 H^+ on the right hand side of the second half reaction will cancel 6 of the 14 H^+ on the left hand side of the first half reaction. These cancellations are shown below:

$$\cancel{6\ e^-} + 8\ \cancel{14}\ H^+ + Cr_2O_7^{2-} \rightarrow 2\ Cr^{3+} + 4\ \cancel{7}\ H_2O$$

$$\cancel{3\ H_2O} + 3\ NO_2^- \rightarrow 3\ NO_3^- + \cancel{6\ H^+} + \cancel{6\ e^-}$$

Sum the two half reactions together to obtain the balanced net ionic equation:

$$8H^+ + Cr_2O_7^{2-} + 3\ NO_2^- \rightarrow 2\ Cr^{3+} + 3\ NO_3^- + 4\ H_2O$$

Finally, the most important step: check the final equation for mass and charge balance. If mass and charge balance has been achieved, the equation cannot be wrong! In this case, mass balances (8H, 2Cr, 13 O, 3N are found on both sides of the equation), and charge balances (a net charge of +3 is found on both sides of the equation).

The steps are summarized on the next page and are followed by a few problems for you to try. The most common step omitted by students is step # 2. Omitting this step will often lead to errors in the number of O's or lack of charge balance.

If you find your final equation is not balanced, it is usually best to start over. Finding your error may be time consuming on a test. Go work another problem and then come back to the balancing so that you won't repeat your previous error while balancing the equation.

SUMMARY OF STEPS

1. Split the equation into two half reactions.

2. Balance any atom other than O or H first.

3. Balance O's using H_2O. Add as many waters as needed to balance the oxygens on the side deficient in oxygen.

4. Balance H's using H^+. Add as many H^+ ions as needed to the side deficient in H.

5. The mass should now be balanced. To balance the charge, determine the charge on each side of the reaction, and add as many electrons to the more positive side as needed to make the charge the same on both sides.

6. Repeat steps 1 through 4 for both half reactions.

7. If the number of electrons lost does not equal the number of electrons gained, find the common multiple and multiply each half reaction by the necessary factor.

8. Sum both half reactions to obtain the balanced, net ionic reaction. In many cases, look for H^+ ions and H_2O molecules to cancel.

9. Check the final equation for mass and charge balance.

Note: If you wish to express H^+ as H_3O^+ then change the number of H^+ into the same number of H_3O^+ and add that same number of H_2O to the opposite side of the equation.

For example:

$$8\ H^+ + Cr_2O_7^{2-} + 3NO_2^- \rightarrow 2\ Cr^{3+} + 3\ NO_2^- + 4\ H_2O$$

becomes

$$8\ H_3O^+ + Cr_2O_7^{2-} + 3\ NO_2^- \rightarrow 2\ Cr^{3+} + 3\ NO_2^- + 12\ H_2O$$

4.4. BALANCING REDOX REACTIONS IN BASE SOLUTION

You can balance redox reactions in base solution in almost the same way as if they were in acid solution. In fact, initially we will assume the reaction is taking place in acid solution but eventually switch over to base. We'll go through the sequence of steps one at a time using a sample equation.

Suppose you wanted to balance the following equation:

$$MnO_4^- + CN^- \rightarrow MnO_2 + CNO^- \text{ (in base)}$$

The first step is to split this equation into two half reactions. One half reaction will show the reduction and the other will show the oxidation. It is not important to initially know which half reaction is which.

$$MnO_4^- \rightarrow MnO_2$$
$$CN^- \rightarrow CNO^-$$

We'll deal with one half reaction at a time, starting with the half reaction for permanganate ion. Check the balance of any atom other than O or H first. In this case the manganese atoms are balanced as written:

$$MnO_4^- \rightarrow MnO_2$$

Next, balance O's using H_2O as if in acid solution by adding H_2O's as necessary to the side deficient in O. In this case, 2 H_2O's are needed on the right hand side of the half reaction:

$$MnO_4^- \rightarrow MnO_2 + 2\ H_2O$$

To balance H's, add as many H^+ ions as needed to the side deficient in H, as if in acid solution. In this case, 4 H^+ are needed on the left hand side of the half reaction:

$$4\ H^+ + MnO_4^- \rightarrow MnO_2 + 2\ H_2O$$

Now "reality" comes into the picture. We should switch over to base solution by adding the same number of OH^- ions as we have H^+ ions to both sides of the half reaction. In this case, 4 OH^- ions are added to both sides of the half reaction:

$$4\ OH^- + 4\ H^+ + MnO_4^- \rightarrow MnO_2 + 2\ H_2O + 4\ OH^-$$

The H^+ is now "removed" from the equation by taking the H^+ ions and OH^- ions found on one side of the half reaction and forming H_2O's. In this case, 4 H^+ ions and 4 OH^- ions make 4 H_2O molecules:

$$4\ H_2O + MnO_4^- \rightarrow MnO_2 + 2\ H_2O + 4\ OH^-$$

Notice how some water molecules may be cancelled. There are 4 H_2O's on the left hand side of the equation, and 2 H_2O's on the right hand side of the reaction. The 2 H_2O's on the right can cancel 2 of the 4 H_2O on the left:

$$2\ H_2O + MnO_4^- \rightarrow MnO_2 + 4\ OH^-$$

Mass balance has now been achieved. Charge balance comes next. Determine the net charge on each side of the half reaction and add electrons to the more positive side so that the charge becomes the same on both sides. In this case, the net charge on the left and side of the half reaction is -1; on the right hand side, the net charge is -4. A charge of -1 is more positive than a charge of -4, therefore, add 3 electrons to the left hand side so that the charge is -4 on both sides:

$$3\ e^- + 2\ H_2O + MnO_4^- \rightarrow MnO_2 + 4\ OH^-$$

This half reaction, showing the reduction, is now both mass and charge balanced. You can tell it's a reduction because electrons are being gained (they are a "reactant"). We'll put this half reaction aside for now.

Repeat the previous steps to obtain mass and charge balance for the second half reaction. First, check the balance of any atom other than O or H. In this case, both the C and N are balanced as written:

$$CN^- \rightarrow CNO^-$$

Next, pretending we are carrying out the reaction in acid solution, balance the O using H_2O. In this case, 1 H_2O is needed on the left hand side to balance the O:

$$H_2O + CN^- \rightarrow CNO^-$$

To balance H's, add H^+ to the side deficient in H. In this case, add 2 H^+ to the right hand side of the half reaction:

$$H_2O + CN^- \rightarrow CNO^- + 2\ H^+$$

Now it is time to switch over to base. Recall this is done by adding the same number of OH^- as you have H^+ to both sides of the half reaction. In this case 2 OH^- must be added to both sides:

$$2\ OH^- + H_2O + CN^- \rightarrow CNO^- + 2\ H^+ + 2\ OH^-$$

Convert the 2 H^+ and 2 OH^- on the right hand side to H_2O's:

$$2\ OH^- + H_2O + CN^- \rightarrow CNO^- + 2\ H_2O$$

Cancel H_2O where possible. In this case, the H_2O on the left hand side of the half reaction will cancel one of the H_2O's on the right hand side of the half reaction.

$$2\ OH^- + CN^- \rightarrow H_2O + CNO^-$$

The half reaction is now mass balanced. Next, balance the charge as before by adding the electrons to the more positive side so that the charges are the same on both sides. In this case, the net charge on the left hand side of the half reaction is -3 (2 hydroxides and 1 cyanide); the net charge on the right hand side is -1 (1 cyanate). A charge of -1 is more positive than a charge of -3, so add 2 electrons to the right hand side of the half reaction:

$$2\ OH^- + CN^- \rightarrow CNO^- + H_2O + 2\ e^-$$

This half reaction showing the oxidation is now both mass and charge balanced. Next, we will retrieve the first half reaction and proceed to follow the steps needed to combine them to for the overall reaction. Before we can add the two half reactions to obtain the overall net ionic reaction, the number of electrons lost must equal the number of electrons gained. In this case, 2 electrons are lost and 3 electrons are gained:

$$2\ H_2O + MnO_4^- + 3\ e^- \rightarrow MnO_2 + 4\ OH^-$$

$$2\ OH^- + CN^- \rightarrow CNO^- + H_2O + 2\ e^-$$

We need to find the least common multiple (lcm) of 2 and 3. The lcm, in this case, is 6. Multiply through each half reaction by the factor necessary to obtain the least common multiple. Here, the first half reaction must be multiplied by 2 and the second half reaction by 3:

$$2 \times (\ 2\ H_2O + MnO_4^- + 3\ e^- \rightarrow MnO_2 + 4\ OH^-\ )$$

$$3 \times (\ 2\ OH^- + CN^- \rightarrow CNO^- + H_2O + 2\ e^-\ )$$

The resulting half reactions are:

$$4\ H_2O + 2\ MnO_4^- + 6\ e^- \rightarrow 2\ MnO_2 + 8\ OH^-$$

$$6\ OH^- + 3\ CN^- \rightarrow 3\ CNO^- + 3\ H_2O + 6\ e^-$$

Sum the two half reactions together, cancelling any like terms to obtain the balanced, net ionic reaction. In this case, the 6 electrons will cancel, the 3 H_2O's on the right hand side will cancel 3 of the 4 H_2O's on the left hand side, and the 6 OH^-on the left hand side will cancel 6 of the 8 OH^- on the right hand side:

$$H_2O + 2\ MnO_4^- + 6\ e^- \rightarrow 2\ MnO_2 + 2OH^-$$

$$3\ CN^- \text{-->}\ 3\ CNO^- + 6\ e^-$$

What remains should be the balanced, net ionic equation. The most important step is to check this final equation for mass and charge balance:

$$H_2O + 2\ MnO_4^- + 3\ CN^- \rightarrow 2\ MnO_2 + 2\ OH^- + 3\ CNO^-$$

The mass balances: 2 H, 2 Mn, 9 O, 3 C, and 3 N are found on each side of the reaction. For charge balance, the net charge on the left hand side is -5 (-2 from two permanganate ions and -3 form three cyanide ions), and also -5 on the right hand side (-2 from two hydroxide ions and -3 form three cyanate ions). Since mass and charge balance has been achieved, the reaction must be correctly balanced.

SUMMARY OF STEPS

1. Divide the equation into two half reactions.

2. Balance any atom other than O or H first.

3. Balance O using H $_2$O. Add as many H_2O's as necessary to the side deficient in O.

4. As if with acid solution, balance the H's by adding H^+ to the side deficient in H.

5. Switch over to base by adding the same number of OH^- as there are H^+ to both sides of the half reaction.

6. One side of the half reaction will contain H^+ and OH^-. Convert the n H^+ and n OH^- to n H_2O's.

7. Cancel H_2O molecules where possible.

8. Balance the charge by adding electrons to the more positive side to equal the less positive side.

9. Repeat these steps for the second half reaction.

10. If the number of electrons lost does not equal the number of electrons gained, find the least common multiple and multiply each half reaction by the factor necessary to obtain the least common multiple.

11. Add the two half reactions together, canceling the electrons, and any OH^- and/or H_2O where possible.

12. Check the final equation for mass and charge balance.

4.5. PROBLEMS

4.5.1. REDOX REACTIONS IN ACIDIC SOLUTION:

1. $I^- (aq) + ClO^-(aq) \longrightarrow I_3^-(aq) + Cl^-(aq)$

2. $As_2O_3 (s) + NO_3^- (aq) \longrightarrow H_3AsO_4 (aq) + NO (g)$

3. $Br^- (aq) + MnO_4^- (aq) \longrightarrow Br_2 (l) + Mn^{2+} (aq)$

4. $CH_3OH (aq) + Cr_2O_7^{2-} (aq) \longrightarrow CH_2O(l) + Cr^{3+}(aq)$

5. $Mn^{2+}(aq) + BiO_3^- (aq) \longrightarrow Bi^{3+}(aq) + MnO_4^- (aq)$

6. $S_8(s) + NO_3^-(aq) \longrightarrow SO_3^{2-}(aq) + NO(g)$

7. $H_3AsO_4(aq) + Zn(s) \longrightarrow AsH_3(g) + Zn^{2+}(aq)$

8. $P_4(s) + Cr_2O_7^{2-}(aq) \longrightarrow H_3PO_4(aq) + Cr^{3+}(aq)$

4.5.2. REDOX REACTIONS IN BASIC SOLUTION

9. $Al(s) + MnO_4^-(aq) \longrightarrow MnO_2(s) + Al(OH)_4^-(aq)$

10. $NO_2^-(aq) + Al(s) \longrightarrow NH_3(aq) + AlO_2^-(aq)$

11. $Cr(s) + CrO_4^{2-}(aq) \longrightarrow Cr(OH)_3(s)$

    Note: $Cr(OH)_3$ is found in BOTH half reactions!

12. $MnO_4^-(aq) + S^{2-}(aq) \longrightarrow MnO_2(s) + SO_3^{2-}(aq)$

13. $Cl_2(aq) + Br_2(l) \longrightarrow OBr^-(aq) + Cl^-(aq)$

14. $H_2O_2(aq) + I^-(aq) \longrightarrow IO_3^-(aq)$

    Note: IO_3^- is found in both half reactons!

15. $NO_3^-(aq) + NH_3(aq) \longrightarrow NO_2^-(aq)$

16. $S_8(aq) + MnO_4^-(aq) \longrightarrow SO_4^{2-}(aq) + MnO_2(s)$

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