Sample Oxidation State and Redox Balancing Problems

Rick Sobers’ Lecture Notes

(Last Updated 30 March 2012)

1. Determine the oxidation state of each element in Na₂SO₄

Recognize this is an ionic compound containing two sodium ions, Na⁺, and one sulfate ion, SO₄²⁻.

**Oxygen** has an oxidation state of -2 in this compound.

**Sodium** has an oxidation state of +1 in this compound.

Review the rules for oxidation states before moving on.

To determine the oxidation state of sulfur requires an algebraic equation.

The oxidation state of sulfur is x. The sum of oxidation states equals the total charge.

2 (+1) + 4(-2) + 1x = 0

Can you explain this equation?

x = +6

So the oxidation state of sulfur is +6

2. Repeat problem 1 focusing on the sulfate ion alone, SO₄²⁻

**Oxygen** has an oxidation state of -2 in this compound.

To determine the oxidation state of sulfur requires an algebraic equation.

The oxidation state of sulfur is x. The sum of oxidation states equals the total charge.

4(-2) + 1x = -2

Can you explain this equation?

x = +6

The same result as expected.

3. Determine the oxidation state of each element in calcium phosphate, Ca₃(PO₄)₂.

**Calcium** is a monatomic ion, Ca²⁺, so the oxidation state is the charge +2.

**Oxygen** has an oxidation state of -2 in this compound.

**Phosphorous** is determined by algebraic equation.

3(+2) + 8(-2) + 2x = 0

The oxidation state of phosphorous is +5

Try this again focusing on the phosphate ion, PO₄³⁻:

1x + 4(-2) = -3

x = +5

Sobers’ Notes 1 Sample Redox Problems
4. Determine the oxidation state of hydrogen in each of the following substances.

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>H₂O₂</th>
<th>H₂</th>
<th>NaH</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>+1, hydrogen is typically +1 and fluorine is -1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O₂</td>
<td>+1, this is hydrogen peroxide. It is an exception for oxygen. What must be the oxidation state of oxygen in this compound? *</td>
<td></td>
<td></td>
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<tr>
<td>H₂</td>
<td>0, this is hydrogen as an element. Hydrogen becomes more oxidized or reduced relative to the elemental form</td>
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<tr>
<td>NaH</td>
<td>-1, remember sodium is a metal and in this ionic compound, sodium has a charge of +1. That means hydrogen must be a monatomic ion of opposite charge. That is -1. This is called the hydride ion, H⁻. **</td>
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</table>

* Peroxides are compounds with oxygen single bonds - O=O -. This is a good example of rule #8 (on class handout for oxidation #'s) – lower numbered rules in the list of rules for oxidation states supersede higher number rules. Clearly in H₂O₂ one element must not have it’s usual oxidation state. Hydrogen as a +1 oxidation state is listed as a rule first, before the rule of oxygen having an oxidation state of -2. Of course this doesn’t explain why.

Compare three oxygen containing molecules: O=O H-O H-O-O-H

In oxygen molecule the oxidation state is zero. Oxygen is bonded to another atom of it’s own element. In water the oxygen is bonded to two hydrogen atoms. The oxygen is in reduced form because it is attached to two hydrogen atoms. The oxygen can pull electron density from each. In hydrogen peroxide an oxygen atom is attached to only one hydrogen to pull electron density from. The other bond is two another oxygen atom. So the oxidation state of oxygen in a peroxide is between that of oxygen molecule, 0, and water, -2.

There are other peroxides. Hydrocarbons can replace the hydrogen atoms in hydrogen peroxide. Benzoyl peroxide is a common organic peroxide containing molecule for instance.

** Another example of rule 8 (see handout on oxidation #'s) in the list of rules for assigning oxidation numbers. Rule 2 states that the oxidation state of monatomic ions is equal to the charge of the ion. Later in rule 5 it is stated that hydrogen is usually +1. Rule 2 supersedes rule 5. Of course the physical reason is that the sodium ion is +1 and the hydride ion is -1 in this ionic compound.
5. Balance the following oxidation-reduction reaction in acidic solution.

\[ \text{Cd}(s) + \text{NO}_3^-(aq) \rightarrow \text{Cd}^{2+}(aq) + \text{NO}(g) \]

**First - separate the half reactions.**

\[ \text{Cd}(s) \rightarrow \text{Cd}^{2+}(aq) \]

\[ \text{NO}_3^-(aq) \rightarrow \text{NO}(g) \]

The cadmium is clearly being oxidized through its loss of electrons. The nitrogen can be seen as undergoing reduction for a couple of reasons:

1. Cadmium is being oxidized and this oxidation must be coupled to a reduction. 2. For most elements decreasing the number of bonded oxygen atoms decreases the oxidation-state, as oxygen is more electronegative (fluorine being an exception to this rule). Nitrogen loses two oxygen atoms so it is being reduced.

3. Finally using the rules for determining oxidation numbers shows that nitrogen is going from an oxidation number of +5 to +2.

**Second - balance the cadmium half reaction:**

This type is easy. Just a neutral metal going to an ion involves loss of electrons.

\[ \text{Cd}(s) \rightarrow \text{Cd}^{2+}(aq) + 2e^- \]

**Third - balance the nitrogen half reaction:**

**Step 1 – Balance elements other than hydrogen and oxygen**

Nitrogen is balanced already – no change

\[ \text{NO}_3^-(aq) \rightarrow \text{NO}(g) \]

**Step 2 - Balance oxygen using water molecules**

\[ \text{NO}_3^-(aq) \rightarrow \text{NO}(g) + 2\text{H}_2\text{O} \]

**Step 3 - Balance hydrogen using hydrogen ion H^+**

\[ 4\text{H}^+(aq) + \text{NO}_3^-(aq) \rightarrow \text{NO}(g) + 2\text{H}_2\text{O} \]

**Step 4 - Balance charge using electrons e^-**

\[ 3e^- + 4\text{H}^+(aq) + \text{NO}_3^-(aq) \rightarrow \text{NO}(g) + 2\text{H}_2\text{O} \]

**Fourth - add the half reactions:**

One half reaction has 3 electrons and the other has 2. The lowest common multiple is 6. Multiply each half reaction so that 6 electrons appear in the reaction. Then add them.

\[ [ \text{Cd}(s) \rightarrow \text{Cd}^{2+}(aq) + 2e^- ] \times 3 \]

\[ + [ 3e^- + 4\text{H}^+(aq) + \text{NO}_3^-(aq) \rightarrow \text{NO}(g) + 2\text{H}_2\text{O} ] \times 2 \]

\[ 8\text{H}^+(aq) + 2\text{NO}_3^-(aq) + 3\text{Cd}(s) \rightarrow 3\text{Cd}^{2+}(aq) + 2\text{NO}(g) + 4\text{H}_2\text{O} \]
6. Balance the following oxidation-reduction reaction in acidic solution.

$$\text{HNO}_3(\text{aq}) + \text{H}_3\text{AsO}_3(\text{aq}) \rightarrow \text{NO}(\text{g}) + \text{H}_3\text{AsO}_4(\text{aq})$$

Before starting this problem let’s take a look at the reacting species. Nitric acid is a strong acid. It is acceptable to write the formula for the unionized form, HNO$_3$. However it is also appropriate to use the ionized form. In this case the nitrate ion, NO$_3^-$, is the reacting species and H$^+$ appears in the equation while balancing the reaction. It is realized of course that nitric acid is a source of the “H$^+$” ion.

$$\text{NO}_3^-(\text{aq}) + \text{H}_3\text{AsO}_3(\text{aq}) \rightarrow \text{NO}(\text{g}) + \text{H}_3\text{AsO}_4(\text{aq})$$

As for the arsenous acid we might consider doing the same thing. However arsenous acid, H$_3$AsO$_3$, is a weak acid and in a solution containing nitric acid, a strong acid, the arsenous acid will be in its unionized form due to Le Châtelier’s principle:

$$\text{H}_3\text{AsO}_3(\text{aq}) \rightleftharpoons \text{H}^+ (\text{aq}) + \text{H}_2\text{AsO}_3(\text{aq})$$

So it is best to balance the equation using the unionized form.

First - separate the half reactions.

NO$_3^-(\text{aq}) \rightarrow \text{NO}(\text{g})$  \hspace{2cm} H$_3$AsO$_3(\text{aq}) \rightarrow \text{H}_3\text{AsO}_4(\text{aq})$

Second - balance the nitrogen half reaction:

This reaction was balanced in problem #5.

$$3e^- + 4H^+(aq) + \text{NO}_3^-(aq) \rightarrow \text{NO}(g) + 2\text{H}_2\text{O}$$

Third - balance the arsenic half reaction:

Step 1 – Balance elements other than hydrogen and oxygen

Arsenic is balanced already – no change

$$\text{H}_3\text{AsO}_3(\text{aq}) \rightarrow \text{H}_3\text{AsO}_4(\text{aq})$$

Step 2 - Balance oxygen using water molecules

$$\text{H}_2\text{O} + \text{H}_3\text{AsO}_3(\text{aq}) \rightarrow \text{H}_3\text{AsO}_4(\text{aq})$$

Step 3 - Balance hydrogen using hydrogen ion H$^+$

$$\text{H}_2\text{O} + \text{H}_3\text{AsO}_3(\text{aq}) \rightarrow \text{H}_3\text{AsO}_4(\text{aq}) + 2\text{H}^+(aq)$$

Step 4 - Balance charge using electrons e$^-$

$$\text{H}_2\text{O} + \text{H}_3\text{AsO}_3(\text{aq}) \rightarrow \text{H}_3\text{AsO}_4(\text{aq}) + 2\text{H}^+(aq) + 3e^-$$

Fourth - add the half reactions:

One half reaction has 3 electrons and the other has 2. The lowest common multiple is 6. Multiply each half reaction so that 6 electrons appear in the reaction. Then add them.

$$[3e^- + 4H^+(aq) + \text{NO}_3^-(aq) \rightarrow \text{NO}(g) + 2\text{H}_2\text{O}] \times 2$$

$$[\text{H}_2\text{O} + \text{H}_3\text{AsO}_3(\text{aq}) \rightarrow \text{H}_3\text{AsO}_4(\text{aq}) + 2\text{H}^+(aq) + 3e^-] \times 3$$

$$6e^- + 8H^+ + 2\text{NO}_3^- + 3\text{H}_2\text{O} + 3\text{H}_3\text{AsO}_3 \rightarrow 2\text{NO}(g) + 4\text{H}_2\text{O} + \text{H}_3\text{AsO}_4 + 6H^+ + 6e^-$$

(All species assumed aqueous unless noted. Water is of course liquid)

Cancel Common Species: $2\text{H}^+ + 2\text{NO}_3^- + 3\text{H}_3\text{AsO}_3 \rightarrow 2\text{NO}(g) + \text{H}_2\text{O} + 3\text{H}_3\text{AsO}_4$
7. Balance the following oxidation-reduction reaction in basic solution:

\[ \text{Cr(OH)}_3(s) + \text{ClO}_3^-(aq) \rightarrow \text{CrO}_4^{2-}(aq) + \text{Cl}^-(aq) \]

It appears that chlorine is being reduced and chromium is being oxidized. Can you explain? In the work that follows assume all species are aqueous unless noted. Water is liquid of course.

**First - separate the half reactions.**

\[
\text{Cr(OH)}_3(s) \rightarrow \text{CrO}_4^{2-}(aq) \quad \text{ClO}_3^-(aq) \rightarrow \text{Cl}^-(aq)
\]

**Second - balance the chromium half reaction:**

**Step 1 – Balance elements other than hydrogen and oxygen**

Chromium is balanced already:

\[ \text{Cr(OH)}_3(s) \rightarrow \text{CrO}_4^{2-} \]

**Step 2 - Balance oxygen using water molecules**

\[ \text{H}_2\text{O} + \text{Cr(OH)}_3(s) \rightarrow \text{CrO}_4^{2-} \]

**Step 3 - Balance hydrogen using hydrogen ion \( \text{H}^+ \)**

\[ \text{H}_2\text{O} + \text{Cr(OH)}_3(s) \rightarrow \text{CrO}_4^{2-} + 5\text{H}^+ \]

**Step 4 - Balance charge using electrons \( e^- \)**

\[ \text{H}_2\text{O} + \text{Cr(OH)}_3(s) \rightarrow \text{CrO}_4^{2-} + 5\text{H}^+ + 3e^- \]

**Third - balance the chlorine half reaction:**

**Step 1 – Balance elements other than hydrogen and oxygen**

Chlorine is balanced already:

\[ \text{ClO}_3^- \rightarrow \text{Cl}^- \]

**Step 2 - Balance oxygen using water molecules**

\[ \text{ClO}_3^- \rightarrow \text{Cl}^- + 3\text{H}_2\text{O} \]

**Step 3 - Balance hydrogen using hydrogen ion \( \text{H}^+ \)**

\[ 6\text{H}^+ + \text{ClO}_3^- \rightarrow \text{Cl}^- + 3\text{H}_2\text{O} \]

**Step 4 - Balance charge using electrons \( e^- \)**

\[ 6e^- + 6\text{H}^+ + \text{ClO}_3^- \rightarrow \text{Cl}^- + 3\text{H}_2\text{O} \]

Continued on next page…
Fourth - add the half reactions:

\[
\begin{align*}
[H_2O + Cr(OH)_3(s) & \rightarrow CrO_4^{2-} + 5H^+ + 3e^-] \times 2 \\
[6e^- + 6H^+ + ClO_3^- & \rightarrow Cl^- + 3H_2O] \times 1
\end{align*}
\]

\[2H_2O + 2Cr(OH)_3(s) + 6H^+ + ClO_3^- \rightarrow 2CrO_4^{2-} + 10H^+ + Cl^- + 3H_2O\]

Cancel Common species: \[2Cr(OH)_3(s) + ClO_3^- \rightarrow 2CrO_4^{2-} + 4H^+ + Cl^- + H_2O\]

Fifth – modify for basic solution:

\[2Cr(OH)_3(s) + ClO_3^- \rightarrow 2CrO_4^{2-} + 4H^+ + Cl^- + H_2O\]

Since it is basic solution, the hydroxide ion should be in the balanced equation instead of the hydrogen ion.

There are 4 hydrogen ions present. Add 4 hydroxide ions to each side:

\[2Cr(OH)_3(s) + ClO_3^- + 4OH^- \rightarrow 2CrO_4^{2-} + 4H^+ + Cl^- + H_2O + 4OH^-\]

React the hydrogen ions with the hydroxide ions to make water:

\begin{align*}
2Cr(OH)_3(s) + ClO_3^- + 4OH^- & \rightarrow 2CrO_4^{2-} + 4H^+ + Cl^- + H_2O + 4OH^- \\
2Cr(OH)_3(s) + ClO_3^- + 4OH^- & \rightarrow 2CrO_4^{2-} + Cl^- + H_2O + 4H_2O
\end{align*}

If there are already water molecules on the same side (as in this case), combine them with a new coefficient equal to the sum of the original. If there were water molecules already in the equation but on the other side then the water molecules would be canceled so that they only appear on one side.

\[2Cr(OH)_3(s) + ClO_3^- + 4OH^- \rightarrow 2CrO_4^{2-} + Cl^- + 5H_2O\]

Another method:

Make use of the following equation for the auto-ionization of water. Write it in the forward or reverse direction and multiply by the number of hydrogen ions in the redox reaction balanced for acidic conditions.

\[
\begin{align*}
\text{Auto-ionization of water equations:} \\
H_2O & \rightarrow H^+ + OH^- \\
H^+ + OH^- & \rightarrow H_2O
\end{align*}
\]

Equation balanced for acid solution:

\[2Cr(OH)_3(s) + ClO_3^- \rightarrow 2CrO_4^{2-} + 4H^+ + Cl^- + H_2O\]

Auto-ionization equation (reverse form):

\[\{H^+ + OH^- \rightarrow H_2O\} \times 4\]

Sum of the two after canceling hydrogen ions and combining or canceling water:

\[2Cr(OH)_3(s) + ClO_3^- + 4OH^- \rightarrow 2CrO_4^{2-} + Cl^- + 5H_2O\]

(Same result)
8. Balance the following oxidation-reduction reaction in acidic solution:

\[ \text{I}_2(s) \rightarrow \text{I}^- + \text{IO}_3^- \]

This reaction is a disproportionation reaction. That is a reaction in which one element is simultaneously oxidized and reduced. A better way to put it is that some atoms of the element are oxidized while some are reduced.

This type of problem is no different than other problems that ask to balance an oxidation-reduction reaction. The mental road block that usually prevents people from answering this kind of problem is the failure to recognize that the same chemical species can appear in BOTH half reactions. In this reaction iodine, initially present as \( \text{I}_2 \), is oxidized and so belongs in the oxidation half reaction. Iodine is also reduced so \( \text{I}_2 \) also appears in the reduction half reaction.

In this reaction iodide ion, \( \text{I}^- \), is more reduced than the elemental form. The iodate ion contains more oxygen than the elemental form of iodine so the iodine in the iodate ion has been oxidized.

**First - separate the half reactions.**

\[ \begin{align*}
\text{I}_2(s) & \rightarrow \text{I}^- \\
\text{I}_2(s) & \rightarrow \text{IO}_3^- 
\end{align*} \]

**Second - balance the reduction half reaction:**

**Step 1 – Balance elements other than hydrogen and oxygen**

\[ \text{I}_2(s) \rightarrow 2\text{I}^- \]

**Step 2 - Balance oxygen using water molecules**

\[ \text{I}_2(s) \rightarrow 2\text{I}^- \]

**Step 3 - Balance hydrogen using hydrogen ion H^+**

\[ \text{I}_2(s) \rightarrow 2\text{I}^- \]

**Step 4 - Balance charge using electrons e^-**

\[ 2e^- + \text{I}_2(s) \rightarrow 2\text{I}^- \]
Third - balance the oxidation half reaction:
Step 1 – Balance elements other than hydrogen and oxygen
I_2(s) \rightarrow 2IO_3^-

Step 2 - Balance oxygen using water molecules
6H_2O + I_2(s) \rightarrow 2IO_3^-

Step 3 - Balance hydrogen using hydrogen ion H^+
6H_2O + I_2(s) \rightarrow 2IO_3^- + 12H^+

Step 4 - Balance charge using electrons e^-
6H_2O + I_2(s) \rightarrow 2IO_3^- + 12H^+ + 10e^-

Fourth - add the half reactions:

\[
\begin{align*}
[2e^- + I_2(s) & \rightarrow 2I^-] \times 5 \\
[6H_2O + I_2(s) & \rightarrow 2IO_3^- + 12H^+ + 10e^-] \times 1
\end{align*}
\]

This reaction can be divided by 2 to get the smallest integers possible:
3H_2O + 3I_2(s) \rightarrow 5I^- + 6H^+ + IO_3^-

(Note: if you divide by 2, remember that as written 5 electrons are now transferred instead of 10. This will become important in later problems.)

In an acidic environment the reverse reaction is clearly favored. (Think Le Châtelier).

The reaction in this direction is favored under basic conditions. The reaction can be written for those conditions by adding hydroxide to each side:

\[
\begin{align*}
3H_2O + 3I_2(s) + 6OH^- & \rightarrow 5I^- + 6H^+ + IO_3^- + 6OH^-
\end{align*}
\]

Combine H^+ and OH^-:
3H_2O + 3I_2(s) + 6OH^- \rightarrow 5I^- + 6H_2O + IO_3^-

Cancel water from each side:
3I_2(s) + 6OH^- \rightarrow 5I^- + 3H_2O + IO_3^-
9. Use the activity series to determine whether the following displacement reactions will occur.

a. Al + CaBr₂

The question asks whether Aluminum will give electrons to calcium to form aluminum ion and calcium metal. It is always good to think of what the reaction will be if the activity series indicates it will occur and then decide if it will occur or not.

If this reaction occurs:

\[
\begin{align*}
\text{Al} & \rightarrow \text{Al}^{3+} + 3e^- \quad \text{Ca}^{2+} + 2e^- \rightarrow \text{Ca} \\
\text{Net:} & \quad 2\text{Al} + 3\text{Ca}^{2+} \rightarrow 2\text{Al}^{3+} + 3\text{Ca}
\end{align*}
\]

(The half reactions were multiplied to cancel electrons).

Checking the activity series:

…Ba>Ca>….Mg>Al>Zn>…

Meaning calcium, Ca, prefers to lose electrons more than aluminum does.

We are comparing a choice between Al³⁺/Ca vs. Al/Ca²⁺

The Al/Ca²⁺ combination is preferred.

The preferred combination already exists.

**So no reaction occurs.**

The activity series indicates calcium is a stronger reducing agent than aluminum. Calcium places electrons on other species more easily than aluminum does. Aluminum is therefore a stronger oxidizing agent. It removes electrons from other species more easily than calcium does.
b. Zn + Ag_2S  (the zinc would end up as Zn^{2+})

If this reaction occurs:
\[ \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \quad \text{Ag}^+ + e^- \rightarrow \text{Ag} \]

Net: Zn + 2Ag^+ \rightarrow Zn^{2+} + 2Ag

The following combinations are being compared:
Zn/Ag^+ vs. Zn^{2+}/Ag

The activity series indicates that Zn^{2+}/Ag is the preferred combination. Zinc is the stronger reducing agent of the two and silver is the stronger oxidizing agent of the two.

The preferred combination represents the products of this reaction above rather than the starting materials.

So a reaction will occur: Zn + 2Ag^+ \rightarrow Zn^{2+} + 2Ag

A comment on these activity series problems: Sometimes problems of this sort found in textbooks are written without giving thought to other possible reactions. For instance it is possible to find problems that ask whether potassium metal will displace sodium ion (K + NaCl). In water both metals react vigorously to form ions. So to ask this question about the metals in an aqueous state is meaningless. However it is possible to consider potassium metal being added to molten sodium chloride for instance.

Similarly the problems asked here are not without complication of further chemistry. For instance in part a, had the reaction occurred the expected product might have been AlBr_3. This is a good first guess at the expected product. However aluminum bromide actually has covalent bonding and exists as Al_2Br_6. Furthermore if this product formed in water it would undergo hydrolysis to form HBr and aluminum hydroxide. So perhaps the expected reaction, had this been indicated by the activity series, would not have been accurate. However the activity series does indicate whether aluminum will displace another metal, if not all the subsequent chemistry.

Finally both zinc and silver sulfide are insoluble so the reaction in part b would not be silver precipitating out of an aqueous solution to be replaced by zinc going into solution as an ion. This reaction would have to take place in the molten state.