

Chapter 13

AQUEOUS REACTIONS, Part 3

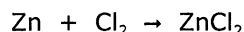
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We now turn to oxidation-reduction reactions. Just like the prior reaction types, such reactions are not restricted to the water world and they occur under a multitude of circumstances. Given the magic of water, however, and its ability to dissociate things, these reactions commonly occur in aqueous solution involving individual ions and/or whole compounds. Oxidation-reduction is a very different type of reaction than what we've been working with so far. Oxidation-reduction reactions are also called redox ("redox"), which is a contraction of reduction-oxidation.

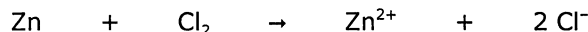
13.1 Redox

Redox reactions involve a net transfer of electrons from one atom or from one chemical unit to another. In some cases, the transfer involves a direct exchange of electrons between reactants. In other cases, there can be an exchange of atoms between chemical units and this results in a change in electron count for one or more of the atoms in those units; those cases can be more complicated, but we will see how to assess the overall, net transfer. There are two parts to redox, an oxidation part and a reduction part. Oxidation is the act of losing electrons and reduction is the act of gaining electrons. These processes must always occur together. One chemical unit loses electrons, another chemical unit gains those electrons.

When elements and/or monatomic ions are involved as reactants or as products or as both, then this electron transfer business is fairly easy to see. Consider again the reaction of metallic zinc with elemental chlorine from Chapter 6.

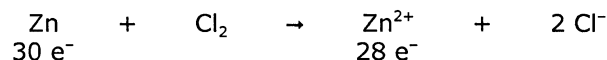


For this discussion, let's look at the individual ions of the zinc chloride product.



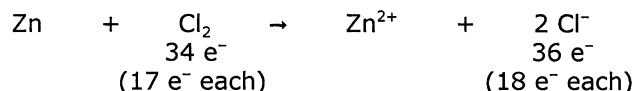
We can examine this as an aqueous or nonaqueous reaction but it really doesn't matter right now, so I'm not bothering with phases. Just keep your eyeballs on the electrons. Count them up for each item in the equation.

- ▶ Each zinc atom within the metal begins with 30 electrons. Each zinc ion has 28 electrons.



Each zinc atom in the network has lost two electrons in the process. This is oxidation. We say the zinc was oxidized.

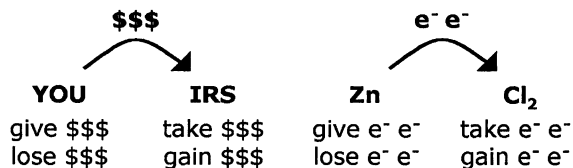
- ▶ Each chlorine atom in the diatomic chlorine molecule begins with 17 electrons. Each chloride ion has 18 electrons.



Each chlorine gained one electron in the process. This is reduction. We say the chlorine was reduced.

For the equation as written, two electrons were lost and two were gained. THE LOSS MUST EQUAL THE GAIN. Always. Always. Always. I'll be harping on this point.

Think of redox as a lose/gain or as a give/take relationship. There are many of these in your life. Some are by choice. Some are not, such as those with the IRS. We can say that you "give \$\$\$" to the IRS or that you "lose \$\$\$" to the IRS. We can say that the IRS "takes \$\$\$" or the IRS "gains \$\$\$". For the present redox example, we can say that Zn "gives e⁻'s" or Zn "loses e⁻'s". We can say that Cl₂ "gains e⁻'s" or Cl₂ "takes e⁻'s". Give/take or lose/gain: they're used in the same context. The essential feature is the transfer of something (\$ or e⁻) from one unit to another. By the way, these are not willful acts on the part of the giver. I would rather keep my \$\$\$, but the IRS takes the money regardless. The zinc would rather keep its electrons, but the Cl₂ is taking them regardless.



Using the Zn/Cl₂ reaction, let's summarize some of the terminology.

The act of losing electrons = oxidation. This happened to Zn.

The act of gaining electrons = reduction. This happened to Cl₂.

These are the acts of redox. It is important that you distinguish these as the acts of redox because now I will explain to you the agents of redox. The reactants are the agents of redox. The agents of redox are the causers: they cause the act on another reactant.

Zn was oxidized. It was caused by Cl₂. Therefore Cl₂ is the "oxidizing agent".

Cl₂ was reduced. It was caused by Zn. Therefore Zn is the "reducing agent".

Often, the agent names are contracted. Oxidizing agent becomes "oxidant". Reducing agent becomes "reductant". These are common contractions.

Warning! This terminology can be confusing. You must understand the distinction between the acts and the agents. The reason for this is that they appear to contradict each other, but they really don't. Notice how this can happen.

Zn undergoes oxidation but it is the reducing agent.

Cl₂ undergoes reduction but it is the oxidizing agent.

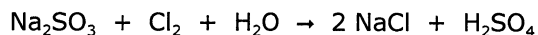
To avoid confusion, remember that THE AGENT CAUSES THE ACT ON ANOTHER REACTANT. Now, let's summarize these points so far.

The oxidizing agent oxidizes another reactant. It does this when it takes (gains) the electrons from that other reactant. Since it gains the electrons, the oxidant is reduced in the process.

The reducing agent reduces another reactant. It does this when it gives (loses) the electrons to that other reactant. Since it loses the electrons, the reductant is oxidized in the process.

For many students, this terminology takes some time to get used to. You just need to work with it.

This Zn/Cl₂ example is about as easy as they get. Like I said upstairs, redox involving monatomic and elemental forms tends to be straightforward. For polyatomic ions and for molecular compounds, redox can be more difficult to interpret. Consider the following aqueous reaction.



Now consider the net ionic equation. The sodium ions are spectators.



For this reaction, who is the oxidant and who is the reductant, and who is gaining the electrons and who is losing the electrons? Look at it first. Can you tell? There is one clue based on the prior example. We again have Cl₂ as a reactant and Cl⁻ as a product, and, sure enough, Cl₂ is grabbing electrons again. Who is losing the electrons? Who is the reducing agent? Who is being oxidized? All three who's are the same.

Later, I will show you how to know who but, for now, I will tell you that it's the sulfite ion. There is a technical way of determining these things and that method relies on a specific system of how to count electrons depending on the electron distribution and bonding in a chemical unit. That leads to a new and very useful parameter, "oxidation number".

13.2 Oxnos

An oxidation number is a numerical value which is assigned to every atom in a chemical unit according to that atom's electronic arrangement within that unit. Oxidation number is often abbreviated as ON. Furthermore, since "nos." is an abbreviation for "numbers", oxidation numbers are sometimes called oxnos, used as singular or plural. We will see the technical counting system for assigning oxidation numbers in Section 27.3 after we get into electronic arrangements, but we can't go there yet. For now, we work with a set of Guidelines for assigning oxidation numbers. These Guidelines are not perfect, but they are good enough for where we are now, including for our current interest in interpreting redox processes. Here are the Guidelines; variations are known and your instructor may choose a different set.

GUIDELINES FOR ASSIGNING OXIDATION NUMBERS

1. All atoms in an elemental form are assigned ON = 0.
2. The ON for a monatomic ion is the same as the ion charge.
3. The sum of all ONs of all atoms within a neutral compound must equal zero. The sum of all ONs of all atoms in an ion must equal the charge of the ion.

4. The ON for H is usually +1, except as above.
5. The ON for O is usually -2, except as above.
6. The ON for a halogen is usually -1, except as above.

Let me make three points. First of all, note that an oxidation number is an assigned number which is based on a specific system of counting. An oxidation number is not the same as a chemical charge, although it is possible for their values to happen to be the same. Secondly, remember that oxnos is assigned to each atom in a chemical unit; it's a number per atom. Thirdly, I can tell you that Guidelines 1, 2 and 3 are firm rules, even in the technically correct method. Number 3 is a biggie; it's used a lot and it's called the "sum rule". It's always true. Guidelines 4, 5 and 6 are given in terms of priorities; these are very usually correct. ("Very usually" does not mean always.) Sometimes 4, 5 or 6 may conflict with Guidelines 1, 2 or 3, but then 1, 2 and 3 will always take priority. Even 4, 5 or 6 can conflict with each other, so remember that their priorities follow the numerical sequence $4 > 5 > 6$. Even with all these stipulations, there can yet be exceptions to 4, 5 and 6. So don't get your dander riled if you see something that doesn't fit. They're guidelines, remember?

Let's do some examples.

- Zn This is an elemental form. Guideline 1 applies. Each Zn atom is assigned ON = 0.
- O₂ Ditto. Each O atom in the molecule is assigned an oxnos of zero.
- He Another elemental form. The helium atom is assigned an oxnos of zero.
- Zn²⁺ This is a monatomic ion. Guideline 2 applies. Zn is assigned oxnos = +2.
- O²⁻ Another monatomic ion. The O is assigned an oxnos of -2.
- Na⁺ Ditto. ON for Na = +1.

Now let's go to bigger formulas.

- H₂O Guidelines 1 and 2 do not apply here. Guideline 3 always applies, but it doesn't give us anything to start with. Guideline 4 does give us a starting point: H is assigned +1. Then, according to Guideline 5, oxygen is assigned -2. Notice that the sum rule (Guideline 3) is obeyed: there are two H's at +1 each and one O at -2, for a sum of zero. We can write this as the following.

$$2 (\text{oxnos of H}) + 1 (\text{oxnos of O}) = 0$$

$$2 (+1) + 1 (-2) = 0$$

A zero sum is required for every neutral compound.

- NH₃ Guideline 4 is again the starting point: H is +1. There is no specific guideline for N, but we can now bring in the algebraic sum rule; here, the sum rule states the following.

$$1 (\text{oxnos of N}) + 3 (\text{oxnos of H}) = 0$$

Since H was assigned +1, we have

$$1 (\text{oxnos of N}) + 3 (+1) = 0$$

and from there we solve for the oxnos of N: it's -3. This illustrates why the sum rule is so important. Since it applies to everything, it can be used to find the oxidation numbers of atoms of many different elements.

- CuCl₂ This is an ionic compound composed of monatomic ions, so we go by charges as per Guideline 2. Cl⁻ has oxnos -1. Although copper is a variable charge cation, the formula requires Cu²⁺ so it has oxnos +2.
- SO₄²⁻ There is no Guideline specific to S but there is one (#5) for O, so that is where we begin: each O is assigned -2. Now, bring in the sum rule.

$$1 (\text{oxnos of S}) + 4 (-2) = -2$$

Notice in this example that the sum was set to -2 because of the ion charge. If you solve this for S, you will find that the oxnos for sulfur is +6.

- KH Ionic compound, potassium hydride. Let's do the individual ions again. Potassium ion has oxnos of +1, hydride has oxnos of -1. Notice that the latter violates Guideline 4, but that's too bad. Remember the priorities. Guideline 4 is over-ruled by Guideline 2.

- H_2O_2 According to Guidelines 4 and 5, hydrogen is +1 and oxygen is -2. But WHOA! Try fitting those to the sum rule.

$$2(+1) + 2(-2) \neq 0$$

It's not going to happen. You cannot violate Guideline 3, so something has to give. Guideline 4 says H is usually +1 and Guideline 5 says O is usually -2. Guideline 4 has more priority, so we keep H at +1 and we ignore Guideline 5. Now go to the sum rule.

$$2(+1) + 2(\text{oxnos of O}) = 0$$

You will find that the oxnos of each O is -1. This example is hydrogen peroxide. An oxnos of -1 for O is characteristic of peroxide compounds in general.

- $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ Sucrose. Table sugar. We assign +1 each for all hydrogens, -2 each for all oxygens and the sum rule for carbons.

$$12(\text{oxnos of C}) + 22(+1) + 11(-2) = 0$$

You will find that each carbon is assigned an oxnos of 0. Notice that you do not have to be an elemental form to have a zero oxidation number.

- $\text{C}_3\text{H}_4\text{F}_2$ Hydrogens take +1 again. Fluorine is a halogen, so we assign -1 for the F's (Guideline 6). We need the sum rule for the carbons.

$$3(\text{oxnos of C}) + 4(+1) + 2(-1) = 0$$

Solve, and you will find that the carbons have an oxnos of $-2/3$. Oxnos can be fractional at this stage, but it's an artifact of the sum rule. The reason is that, when you solve by the sum rule, you're actually solving for an average. In this compound, all three carbons have different oxnos. One C is +2, one C is -1 and one C is -3. How do you know that? At this stage you can't; I'm just using this to illustrate that you can end up with a fractional oxidation number. If you take the average of +2, -1 and -3, then you get $-2/3$. That's the point I'm trying to make: the sum rule gives an average, and this can give you a fractional oxnos at this stage of the game.

- ClO_4^- O should be -2, and Cl (a halogen) should be -1, but that's another strike against the sum rule.

$$1(-1) + 4(-2) \neq -1$$

No can do. We keep O at -2 since it's Guideline 5 and it has priority over Guideline 6 for Cl. We then invoke the inviolable sum rule.

$$1(\text{oxnos of Cl}) + 4(-2) = -1$$

This leaves us with an oxnos of +7 for chlorine.

Hopefully you can see from these various examples how to assign the oxidation numbers to the different atoms in a range of compounds. The one thing to be really careful about is the sum rule. As you saw in the H_2O_2 and ClO_4^- examples, make sure everybody obeys it. Always.

Your turn. Assign oxidation numbers to each atom in the following.

S_6 S: _____

AsF_3 As: _____ F: _____

$\text{Cr}(\text{NO}_3)_2$ Cr: _____ N: _____ O: _____

$\text{H}_5\text{P}_3\text{O}_8$ H: _____ P: _____ O: _____

KClO K: _____ Cl: _____ O: _____

Here are the answers, scrambled. Each number below goes in one of the blanks above. Figure out which goes where.

-2 1 5 (11)/3 3 -2 0 1 -1 2 1 -2

13.3 Uses of oxnos

Now let's go back and apply oxidation numbers to redox processes.

Consider the reaction of chromium(II) ion with elemental iodine to produce chromium(III) ion and iodide. Let's spell out that much.



For this reaction, chromium changes oxnos from +2 on the left to +3 on the right; each iodine changes from zero to -1. We can describe this reaction as the oxidation of chromium(II) by elemental iodine or the reduction of elemental iodine by chromium(II). Either way is correct.

Now balance the equation. The first response by many people would be to throw a coefficient of two on the iodide.



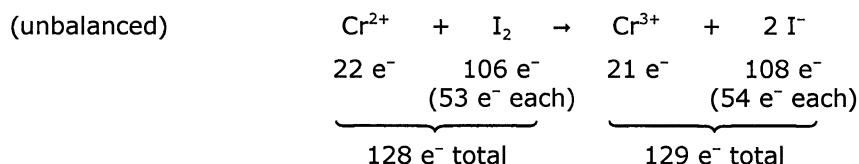
This gives atom balance. Unfortunately, many people would stop there. Sorry, that won't cut the mustard. Those people are wrong. How wrong? It depends on who's grading their exam.

This is where you need to worry about charge balance. In the equation shown, the charges add to +2 on the left and to +1 on the right. That's no good. Notice that you can have atom balance without having charge balance. How can this happen? Let's go back to what I said in Section 11.1.

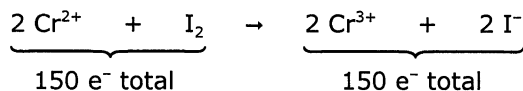
“ Unfortunately, the term "charge balance" is a bit indirect. Charge balance is really electron balance. This is a very important aspect which I am pointing out now, but which I will explain later in Chapters 13 and 14. ”

Later is now.

We've been balancing the atom count all along, but this is actually only a balance of element identities. In the above equation, you have one chromium on each side and you have two iodines on each side. Fine. But element identity lies in the nucleus, which means atom balance does not directly take care of electron balance. Yes, in most cases, electron balance does fall into place with atom balance, but this is not always true with net ionic redox equations. That's because redox involves electron transfer and when electrons transfer between this and that, it's easy to lose track of them. Let's see how this happened in the present example. Count the electrons on both sides of the equation.



There's the problem: there are 128 electrons on the left but 129 electrons on the right. The electrons are not balanced. That's why the charges did not balance even though the atom count did. CHARGE BALANCE IS REALLY ELECTRON BALANCE. Compare that to the correctly balanced equation, which requires a coefficient of two on the chromiums.



You still have atom balance but now you also have charge (electron) balance: charges are +4 on both sides. This is the correct equation. You cannot achieve full balance unless the number of electrons is the same on both sides.

This equation is a very simple case of redox balance, yet it can still be tedious to keep track of all of the electrons. The task becomes horrendous when more complicated reactants and products are involved. Fortunately, systematic methods of balance have been developed to deal with redox equations. This is where we go next.

Problems

1. True or false.
 - a. In a redox reaction, the oxidant is reduced.
 - b. In the combustion of methane, carbon is reduced.

- c. Sulfide ion forms from the oxidation of elemental sulfur.
- d. A redox reaction involves a change in oxidation numbers.
- e. In a redox reaction, the oxidant loses electrons to the reductant.
- f. During a redox reaction, the oxidant's oxidation number increases.
- g. During an oxidation-reduction reaction, the reductant gains one or more electrons.
2. Give the oxidation number of each element in each of the following.
- a. H_3AsO_3 b. NaO_2 c. SnCl_3^- d. $\text{S}_4\text{O}_3^{2-}$ e. HBF_4
3. Give the oxidation number of each element in the following.
- a. CaSiO_3 b. $\text{C}_6\text{H}_4\text{Cl}_2$ c. H_2S_3 d. TeOF_2 e. $(\text{NH}_4)_2\text{SeO}_4$
4. Consider the following equation.
- $$5 \text{Cr}^{2+} + 4 \text{MnO}_4^- + 4 \text{H}_2\text{O} \rightarrow 5 \text{CrO}_4^{2-} + 4 \text{Mn}^{2+} + 8 \text{H}^+$$
- a. Which reactant loses electrons?
- b. Which reactant gains electrons?
- c. What is the oxidant?
- d. What is the reductant?
5. Consider the following equation.
- $$6 \text{SO}_4^{2-} + 6 \text{H}^+ + \text{Br}_2 \rightarrow 3 \text{S}_2\text{O}_6^{2-} + 2 \text{H}_2\text{O} + 2 \text{HBrO}_2$$
- a. Which reactant loses electrons?
- b. Which reactant gains electrons?
- c. What is the oxidant?
- d. What is the reductant?
6. Consider the following equation.
- $$8 \text{V}^{2+} + 3 \text{IO}_6^{5-} + 4 \text{H}^+ \rightarrow 8 \text{VO}_2^+ + 3 \text{I}^- + 2 \text{H}_2\text{O}$$
- a. Which reactant loses electrons?
- b. Which reactant gains electrons?
- c. What is the oxidant?
- d. What is the reductant?