1.2: Redox Reactions

"Oxidation state" implies a description that can change: a metal can go from one oxidation state to another. For example, a Cu(I) can become a Cu(0). It does so by an electron transfer from one place to another. In the case of Cu(I)/Cu(0), an electron would have to be donated by some other species.

A loss of electrons is called an "oxidation", whereas a gain of electrons is called a "reduction" (as immortalized in the mnemonic: LEO the lion goes GER). Since an electron always goes from somewhere to somewhere else, one thing is always oxidized when something else is reduced. (Note that this is a little like proton transfer reactions: a proton is always transferred from one basic site to another, and is never really by itself.) These paired processes are called "reduction-oxidation" reactions, or "redox" for short.

So the reduction of Cu(I) to Cu(0) is just a "half-reaction"; it needs a corresponding oxidation to make it happen. Li could donate an electron, for example, to become Li^+. In a biological setting, a Fe(III) in an important protein may need an extra electron to become Fe(II) in order to do its job (your life may be at stake here). It could get the electron from a nearby Cu(I), which becomes Cu(II).

Exercise 1.2.1

Balance the following half reactions by adding the right number of electrons to one side or the other.

a) Cu → Cu(I) b) Fe(III) → Fe

c) Mn → Mn^{3+} d) Zn^{2+} → Zn

e) F^- → F_2 f) H_2 → H^+

Answer a

a) Cu → Cu^+ + e^-

Answer b

b) Fe^{3+} + 3 e^- → Fe

Answer c

c) Mn → Mn^{3+} + 3 e^-

Answer d

d) Zn^{2+} + 2 e^- → Zn

Answer e

e) 2 F^- → F_2 + 2 e^-

Answer f

f) H_2 → 2 H^+ + 2 e^-

Sometimes, redox reactions work out very neatly: one participant needs an electron or two, and the other participant has one or two electrons to give. For example, a Cu^{2+} ion in need of two electrons to become a Cu atom might get them from a Zn atom, which would become a Zn^{2+} ion.

In other words (or other symbols):

$$\mathrm{Cu^{2+} + 2\,e^- \longrightarrow Cu}$$

$$\mathrm{Zn^{2+} \longrightarrow Zn + 2\,e^-}$$

Adding those together:

$$\mathrm{Cu^{2+} + Zn \longrightarrow Cu + Zn^{2+}}$$

Note that the electrons on each side just cancel each other, much like adding the same thing to both sides of an equals sign.

So, overall, a copper ion could get a couple of electrons from a zinc atom, leaving a copper atom and a zinc ion. Wouldn't the opposite reaction also be possible?

$$Cu + Zn^{2+} \longrightarrow Cu^{2+} + Zn$$

On paper, yes. In reality, it doesn't work as well in this direction. In order to help keep track of what redox reactions are actually able to occur, chemists have compiled something called the activity series of metals. The activity series just lists metals in the order in which they are most likely to give up an electron. Metals appearing at the top of the series give up an electron most easily. Metals at the bottom don't give up electrons so readily.

Metal	Ion Formed	Reactivity with Acids
Cs	Cs^+	reacts with water
Rb	Rb^+	
K	K^+	
Li	Li^+	
Ba	Ba^+	
Sr	Sr^+	
Ca	Ca^{2+}	
Mg	Mg^{2+}	reacts with HCl
Al	Al^{3+}	
Mn	Mn^{2+}	
Zn	Zn^{2+}	
Cr	Cr^{2+}	
Fe	Fe^{2+}	
Cd	Cd^{2+}	
Co	Co^{2+}	
Ni	Ni^{2+}	
Sn	Sn^{2+}	
Pb	Pb^{2+}	
H_2	H^+	
Sb	Sb^{2+}	reacts with oxidizing acids
Bi	Bi^{3+}	(HNO_3, etc)
Cu	Cu^{3+}	
Hg	Hg^{2+}	
Ag	Ag^+	
Au	Au^{3+}	
Pt	Pt^{2+}	

The activity series was put together using a variety of information about redox reactions. Sometimes, maybe one metal was simply placed with another metal ion to see whether the reaction occurred. Often other reactions were studied in order to infer how easily a particular metal would give up its electrons. Some of the trends in the activity series have simple explanations and others do not. We will see later that there are many different factors that govern redox reactions.

We have seen a few reactions in which one metal atom simply transfers an electron or two to another metal ion. Other times, things may be slightly more complicated. There may be an issue of conserving matter, for instance. For example, hydrogen gas, H_2, can be oxidised to give proton, H^+. We can't have more hydrogen atoms before the reaction than afterwards; matter can't just be created or destroyed. To solve that problem, the oxidation of hydrogen gas, H_2, produces two protons, not just one, and so two electrons are involved as well.

Alternatively, two half-reactions may actually involve different numbers of electrons, and so proportions of each half reaction need to be adjusted in order to match the number of electrons properly.

Exercise 1.2.2

Put the following pairs of half reactions together to make a full reaction in each case. Make sure you have balanced the half reactions first.

a) Cu(I) → Cu(II) and Fe(III) → Fe(II) b) Cu(I) → Cu(0) and Ag(0) → Ag(I)

c) F_2 → F^- and Fe → Fe^{3+} d) Mo^{3+} → Mo and Mn → Mn^{2+}

Answer a

a) Cu(I) + Fe(III) → Cu(II) + Fe(II)

Answer b

b) Cu(I) + Ag(0) → Cu(0) + Ag(I)

Answer c

c) 3 F_2 + 2 Fe → 6 F^- + 2 Fe(III)

Answer d

d) 2 Mo^{3+} + 3 Mn → 2 Mo + 3 Mn^{2+}

In many cases, redox reactions do not just involve simple metal ions or atoms. Often, the metal atom is found within a compound or a complex ion. For example, one of the most common oxidizing agents in common use is permanganate ion, MnO_4^-, which is usually converted to manganese dioxide, MnO_2 during a reaction.

That means the half reaction here is:

$$\mathrm{MnO_4^-} \longrightarrow \mathrm{MnO_2}$$

In order to sort out how many electrons are being traded, we need to know the oxidation state of manganese before and after the reaction. That turns out to be Mn(VII) before and Mn(IV) afterwards. That means 3 electrons are added to permanganate to produce manganese dioxide.

Now we have:

$$\mathrm{MnO_4^-} + 3\,\mathrm{e^-} \longrightarrow \mathrm{MnO_2}$$

But now we just have a mass balance problem again. There are oxygen atoms before the reaction that have just disappeared after the reaction. Where could those oxygen atoms have gotten to? On this planet, the simplest answer to that question is always water. So maybe 2 waters were produced as part of the reaction.

That gives us:

$$\mathrm{MnO_4^-} + 3\,\mathrm{e^-} \longrightarrow \mathrm{MnO_2} + 2\,\mathrm{H_2O}$$

Only now we have more problems. First of all, now we have some hydrogen atoms on the right that we didn't have on the left. Where did these things come from? Also, there is this niggling problem of negative charges that we had before the reaction that we don't have after the reaction. Charge, like matter, doesn't just appear or disappear. It has to go someplace, and we have to explain where.

We'll kill two birds with one stone. Maybe some protons were added to the reaction at the beginning, giving us those hydrogen atoms for the water and balancing out the charge.

We are left with:

$$MnO_4^- + 3\,e^- + 4\,H^+ \longrightarrow MnO_2 + 2\,H_2O$$

It all works out. There are four negative charges on the left, and four plus charges, so no charge overall. There are no charges on the right. There is one manganese on the left and on the right. There are four oxygens on the left and on the right. There are four hydrogens on the left and on the right.

An Alternative Situation is Possible

Now let's take a little detour. We're going to go back in time, to the point where we realized we had a problem with our oxygen atoms.

Now we have:

$$MnO_4^- + 3\,e^- \longrightarrow MnO_2$$

But now we just have a mass balance problem again. There are oxygen atoms before the reaction that have just disappeared after the reaction. Where could those oxygen atoms have gotten to? And while we're at it, there are four negative charges on the left and none on the right. Charge doesn't just appear or disappear during a reaction. It has to be balanced.

One solution for this problem involves the production of hydroxide ions, HO^-, during the reaction. Hydroxide ions are pretty common; there are a few in every glass of water. The charge in the reaction would be balanced if four hydroxide ions were produced, and it would explain where those oxygen atoms went.

That gives us:

$$MnO_4^- + 3\,e^- \longrightarrow MnO_2 + 4\,OH^-$$

Now the charge is balanced! But the oxygen atoms aren't. And where did those hydrogen atoms come from?

Well, on this planet, a good source of hydrogen and oxygen atoms is water. Maybe the reaction needs water.

That means:

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

One manganese on each side. Four hydrogens on each side. Six oxygens on each side. Four negative charges on each side. Nothing has appeared or disappeared during the reaction. We know where everything went.

There is actually a shortcut to get to this solution. If we already know how to balance the reaction in acididc media, we just add enough hydroxides to neutralize the acid (H^+ + ^-OH = H_2O). But we have to add those hydroxides *to both sides*. Some of the waters will then cancel out to leave the balanced reaction.

Start with acid

$$MnO_4^- + 3\,e^- + 4\,H^+ \longrightarrow MnO_2 + 2\,H_2O$$

Add base to both sides

$$MnO_4^- + 3\,e^- + 4\,H^+ + 4\,OH^- \longrightarrow MnO_2 + 2\,H_2O + 4\,OH^-$$

Neutralize

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

Cancel the extra waters

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

Now we're back. We have seen two different outcomes to this problem. The moral of the story is that sometimes there is more than one right answer. In the case of redox reactions, sometimes things happen a little differently depending on whether things are occurring under acidic conditions (meaning, in this context, that there are lots of protons around) or in basic conditions (meaning there aren't many protons around but there is hydroxide ion).

Apart from helping us to keep track of things, the presence of acids (protons) and bases (hydroxide ions) in redox reactions are common in reality. For example, batteries rely on redox reactions to produce electricity; the electricity is just a current of electrons trying to get from one site to another to carry out a redox reaction. Many batteries, such as car batteries, contain acid. Other batteries, like "alkaline" batteries, for example, contain hydroxide ion.

? Exercise 1.2.3

Balance the following half reactions. Assume the reactions are in acidic conditions.

a)$MnO_2 \rightarrow Mn(OH)_2$ b) $NO \rightarrow N_2O$

c)$HPO_3^{2-} \rightarrow H_2PO_2^-$ d) $Sn(OH)_6^{2-} \rightarrow HSnO_2^-$

Answer a

a) $MnO_2 + 2\ H^+ + 2\ e^- \rightarrow Mn(OH)_2$

Answer b

b) $2\ NO + 2\ e^- + 2\ H^+ \rightarrow N_2O + H_2O$

Answer c

c) $HPO_3^{2-} + 2\ e^- + 3\ H^+ \rightarrow H_2PO_2^- + H_2O$

Answer d

d) $Sn(OH)_6^{2-} + 2\ e^- + 3\ H^+ \rightarrow HSnO_2^- + 4\ H_2O$

? Exercise 1.2.4

State whether or not a reaction would occur in the following situations.

a. Copper wire is covered in nitric acid.
b. Copper wire is covered in zinc chloride.
c. An aluminum sheet is covered in lead chloride.
d. A silver coin is submerged in hydrochloric acid.
e. calcium metal is dropped in water.
f. an iron bar is dipped in hydrochloric acid.
g. a manganese(II) complex is treated with sodium amalgam
h. chromium metal is covered in water

Answer a

a) yes

Answer b

b) no

Answer c

c) yes

Answer d

d) no

Answer e

e) yes

Answer f

f) yes

Answer g

g) yes

Answer h

h) no

? Exercise 1.2.5

a) Given the standard reduction potentials below (vs. NHE), determine the cell potential for the reduction of O_2 to O_2^- by Cu(I) ion.

$$\mathrm{Cu^{2+} + e^- \longrightarrow Cu^+} \backslash)\backslash(E^\circ = +0.153V$$

$\mathrm{Cu^+ + e^- \longrightarrow Cu} \;\; E^\circ = +0.521V$
$\mathrm{O_2 + e^- \longrightarrow O_2^-} \;\; E^\circ = -0.33V$

b) Is the reaction favored under these conditions?

c) Reactions in the presence of metals often involve substrate binding. Show, with arrows and structures, the substrate binding step that would be involved in this case.

d) Explain how this factor may influence the reduction potential of the oxygen.

e) Explain how the following observation supports your answer.

$$\mathrm{O_2 + H^+ e^- \longrightarrow HO_2} \backslash)\backslash(E^\circ = -0.13V$$

f) Metal ions in biology are usually coordinated by amino acid residues. Show a Cu(I) ion coordinated to two aspartic acid residues and two histidine residues.

g) Explain how this factor may influence the reduction potential of the copper.

Answer a

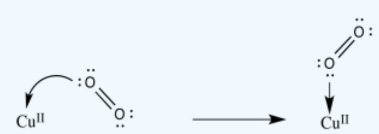
a) E_{rxn} = - 0.153 V - 0.33 V = - 0.483 V

Answer b

b) No.

Answer c

c)



Answer d

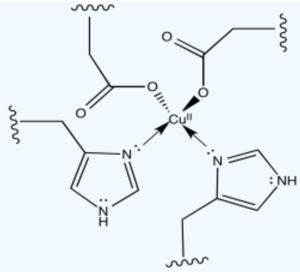
d) The O_2 is activated as an electrophile. Addition of an electron may become easier.

Answer e

e) The reduction potential is 0.2 V more positive when the resulting superoxide ion is stabilised by binding a proton. A similar shift could occur when coordinated to copper.

Answer f

f)



Answer g

The two aspartate ions would make the copper complex less cationic. That may make it easier to remove an electron from the copper complex.

Exercise 1.2.6

The use of Cl_2 in water treatment has been linked to production of harmful chlorinated species in waterways. ClO_2 has been proposed as an alternative, so researchers at Purdue decided to investigate its potential reactivity with common aqueous ions such as iron. (Margerum, *Inorg. Chem.* **2004**, *43*, 7545-7551.)

$$ClO_2 + e^- \longrightarrow ClO_2^- \backslash)\backslash(E^\circ = 0.95V$$

$$Fe^{3+} e^- \longrightarrow Fe^{2+} \backslash)\backslash(E^\circ = 0.77V$$

a. Provide an overall reaction from these half-reactions.
b. Calculate the potential for the overall reaction.
c. Is the reaction favored?
d. Provide a Lewis structure for ClO_2 (connectivity O-Cl-O).
e. Propose a reason for the overall thermodynamics (i.e. favored or disfavored) of the reaction.
f. Does the mechanism seem more likely to proceed by an inner sphere mechanism or by an outer sphere mechanism? Explain why.
g. The addition of ClO_2^- to Fe^{3+} (aq) is known to produce the complex $(H_2O)_5Fe(ClO_2)^{2+}$. This complex has a broad absorption band between 480 and 540 nm in the UV-Visible spectrum. Upon mixing ClO_2 and Fe^{2+} (aq), a broad absorbance appears at 500 nm within 20 ms. Explain this observation.

Answer a

a) $Fe^{2+} + ClO_2 \rightarrow Fe^{3+} + ClO_2^-$

Answer b

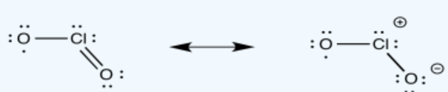
b) $E_{rxn} = 0.95\ V - 0.77\ V = 0.18\ V$

Answer c

c) yes.

Answer d

d)



Answer e

e) ClO_2 has an unpaired electron. ClO_2^- has electrons paired.

Answer f

f) It could be inner sphere: the oxygen in the ClO_2 could coordinate to the iron.

Answer g

g) The mixture quickly forms $(H_2O)_5Fe(ClO_2)^{2+}$ via inner sphere electron transfer.