

7.014 Redox Chemistry Handout

This handout is intended as a brief introduction to redox chemistry. For further reading, consult an introductory chemistry textbook.

Redox reactions involve the transfer of electrons (usually abbreviated e^-) from one molecule to the other. **Reduction** is when a molecule **gains electrons**.

Oxidation is when a molecule **loses electrons**.

(One way to remember this is the mnemonic "LEO says GER", which translates to "Loss of Electrons is Oxidation; Gain of Electrons is Reduction.)

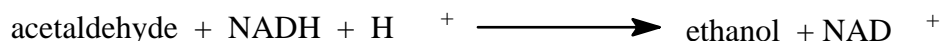
Since electrons cannot exist free in solution, an oxidation must **always** be paired with a reduction; hence the term redox (reduction and oxidation) reaction.

The terminology can be very confusing:

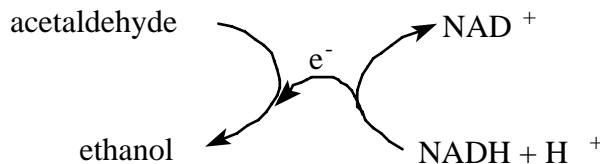
oxidation	loss of e^-
reduction	gain of e^-
oxidizing agent	gains e^- during reaction and is therefore reduced during reaction
reducing agent	loses e^- during reaction and is therefore oxidized during reaction
oxidized form	form of molecule lacking e^-
reduced form	form of the molecule having e^-

There are three ways to represent a redox reaction; these are shown below with a representative biological redox reaction:

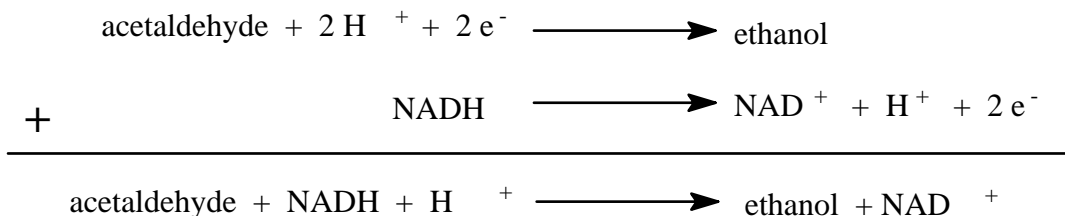
(1) Overall Reaction:



(2) Electron-transfer diagram:



(3) Half-reactions:



In the reaction shown above:

NADH is **oxidized** to NAD⁺
acetaldehyde is **reduced** to ethanol
acetaldehyde is the **oxidizing agent**

NADH is the reducing agent
NADH and ethanol are the reduced forms
NAD⁺ and acetaldehyde are the oxidized forms

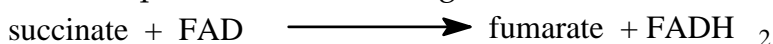
There are two main ways that redox chemistry will be discussed 7.014:

1) Given a redox reaction and the direction it proceeds, what is the e⁻ flow (that is, which molecule is oxidized and which is reduced)?

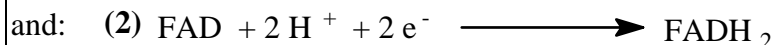
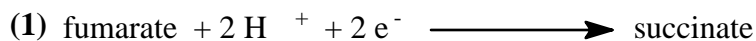
In order to solve this kind of problem, you will need to know how to tell which of the two forms of a given molecule is the reduced form and which is the oxidized form. The easiest way is to:

LOOK IT UP. Use a table of standard oxidation or reduction potentials, like the one on page 6 of this handout. These show the two forms of many common molecules and the redox relationship between them.

For example, take the following reaction from the citric acid cycle:

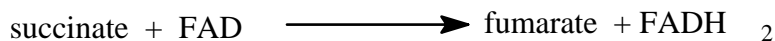
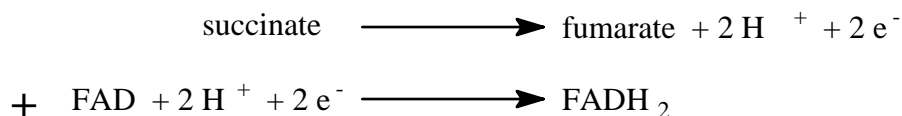


Looking at the chart on page 6 of this handout, you'll find two half reactions relating the compounds in this reaction:



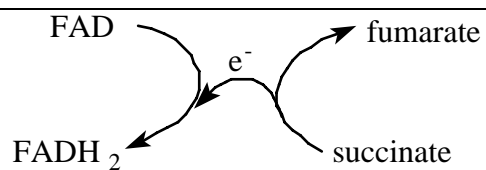
(Don't worry about the E° values just yet.)

These two half reactions add up to the overall reaction if you reverse reaction (1):



Therefore: succinate is oxidized to fumarate
FAD is reduced to FADH₂
FAD is the oxidizing agent
succinate is the reducing agent
succinate and FADH₂ are the reduced forms
fumarate and FAD are the oxidized forms

Or, to use an electron transfer diagram:



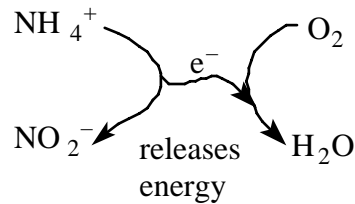
This is the most common method. There is another method in the appendix.

2) Given a redox reaction, in which direction will it proceed spontaneously?

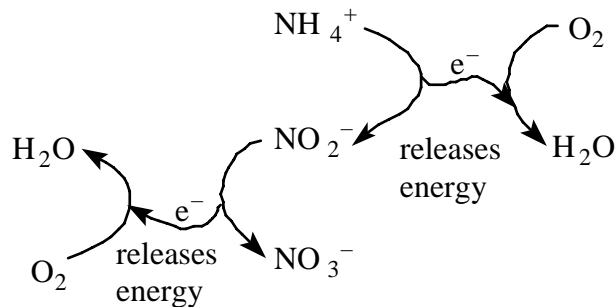
In General:

Different molecules have different tendencies to lose e^- , which reflects the degree to which they are reduced. Their tendency to lose e^- is reflected by their position in the chart on page 6; more reduced molecules are at the lower right of the chart. The more reduced a molecule is, the more potential energy it contains to be released for biological work.

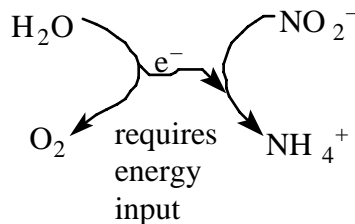
For example:



NH_4^+ is reduced; it has a tendency to release e^- (it is lower in the chart). O_2 is very oxidized; it has a strong tendency to accept e^- . Therefore, if you transfer e^- from NH_4^+ to O_2 ("up the chart"), energy will be released ($\Delta G < 0$). This process can continue as e^- are transferred to O_2 from NO_2^- ; this will also release energy:



On the other hand, the reverse reaction (transfer e^- from H_2O to NO_2^- ; "down the chart") requires energy input to run in the direction shown ($\Delta G > 0$):



This can be put in mathematical terms using the E° values on the chart. This is analogous to figuring out ΔG for a reaction to determine which direction will proceed spontaneously. In the case of redox reactions, the energy of the reaction is measured in volts; each reaction has a standard potential (voltage) E° . ΔG° and E° are related by the Nernst equation:

$$\Delta G'^{\circ} = -nF (\Delta E'^{\circ})$$

Where:

n = number of electrons transferred per reaction

F = the Farraday constant (23 $\frac{\text{kcal}}{\text{volt} \cdot \text{mol}}$)

$$\Delta E'^{\circ} = E'_{(\text{reducing agent})} - E'_{(\text{oxidizing agent})}$$

Note: to determine the direction of a redox reaction, you do not need to use the Nernst equation. You only need to know the sign of $\Delta E'^{\circ}$.

$\Delta E'^{\circ} < 0$ reaction spontaneous <-----

$\Delta E'^{\circ} > 0$ reaction spontaneous ----->

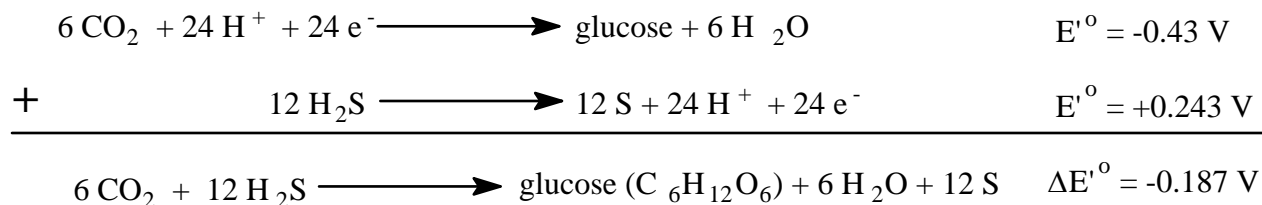
(note that this is the reverse of ΔG)

This is shown for the previous reaction:

In order to arrive at the desired overall reaction:

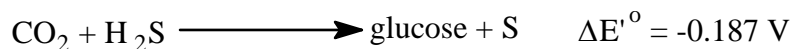
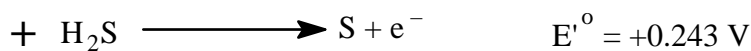
- you must reverse the sign of E'° for a reaction if you reverse the direction of the reaction. Here reaction (2) must be reversed.
- Even though we multiplied the reactions by a constant (6 x reaction 1; 12 x reaction 2) to balance the reaction, we did not multiply E'° even if you multiply the reaction by constant (this is not the same as ΔG).

This is shown below:



Since $\Delta E'^{\circ} < 0$, the reaction is spontaneous to the left (<----). This means that it requires energy input to go to the right - therefore, energy input is required get net glucose synthesis. Since this is a photosynthetic reaction, and a substantial amount of light energy is available, this is no problem.

Note that, since we did not need to balance the reaction to calculate $\Delta E'^{\circ}$, we could have simplified the calculation as follows:



In all cases, you do not have to balance the reaction to find $\Delta E'^{\circ}$.

$\Delta G'^{\circ}$ can be calculated in the following way:

(Note: you will not need to do this for 7.014, it is only included FYI)

This is where balancing the reaction comes in – you have to balance the reaction to get n, the number of e⁻ transferred. In the case of the above reaction n= 24.

$$\Delta G'^{\circ} = -nF (\Delta E'^{\circ})$$

$$\Delta G'^{\circ} = - (24)(23 \frac{\text{kcal}}{\text{volt} \cdot \text{mol}})(- 0.187 \text{ V})$$

$$\Delta G'^{\circ} = +103 \text{ kcals/mol}$$

This is a highly endothermic reaction – therefore a substantial input of is required to get net production of glucose. Since this is a photosynthetic reaction, and a substantial amount of light energy is available, this is no problem.

Final Note:

This overview of oxidation-reduction reactions has been grossly oversimplified to provide the level of understanding necessary to cover the basics of photosynthesis and respiration.

In reality, you will find that all redox reactions are affected by pH and the concentrations of products and reactants. Furthermore, some products or reactants can be further stabilized by other chemical reactions (e.g. Fe³⁺ can precipitate as Fe(OH)₃) which will also alter the equilibrium.

Because of these various circumstances, you may come across situations that do not seem to make sense on the basis of standard redox potentials alone.

The chart on the following page shows the tendency of various compounds to gain or lose e⁻.

A chart of standard E° values (at 25°C and pH 7) is shown below:

Half-Reaction		E° (V)
$1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}^-$	\square H_2O	0.816
$\text{Fe}^{3+} + \text{e}^-$	\square Fe^{2+}	0.771
$\text{NO}_3^- + 6\text{H}^+ + 6\text{e}^-$	\square $1/2\text{N}_2 + 3\text{H}_2\text{O}$	0.75
$\text{NO}_3^- + 2\text{H}^+ + 2\text{e}^-$	\square $\text{NO}_2^- + \text{H}_2\text{O}$	0.421
$\text{NO}_3^- + 10\text{H}^+ + 8\text{e}^-$	\square $\text{NH}_4^+ + 3\text{H}_2\text{O}$	0.36
$\text{NO}_2^- + 8\text{H}^+ + 6\text{e}^-$	\square $\text{NH}_4^+ + 2\text{H}_2\text{O}$	0.34
$\text{CH}_3\text{OH} + 2\text{H}^+ + 2\text{e}^-$	\square $\text{CH}_4 + \text{H}_2\text{O}$	0.17
fumarate + $2\text{H}^+ + 2\text{e}^-$	\square succinate	0.031
$2\text{H}^+ + 2\text{e}^-$	\square H_2 (pH 0)	0.00
oxaloacetate + $2\text{H}^+ + 2\text{e}^-$	\square malate	-0.166
$\text{CH}_2\text{O} + 2\text{H}^+ + 2\text{e}^-$	\square CH_3OH	-0.18
pyruvate + $2\text{H}^+ + 2\text{e}^-$	\square lactate	-0.185
acetaldehyde + $2\text{H}^+ + 2\text{e}^-$	\square ethanol	-0.197
$\text{SO}_4^{2-} + 8\text{H}^+ + 6\text{e}^-$	\square $\text{S} + 4\text{H}_2\text{O}$	-0.20
$\text{SO}_4^{2-} + 10\text{H}^+ + 8\text{e}^-$	\square $\text{H}_2\text{S} + 4\text{H}_2\text{O}$	-0.21
$\text{FAD} + 2\text{H}^+ + 2\text{e}^-$	\square FADH_2	-0.219
$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^-$	\square $\text{CH}_4 + 2\text{H}_2\text{O}$	-0.24
$\text{S} + 2\text{H}^+ + 2\text{e}^-$	\square H_2S	-0.243
$\text{N}_2 + 8\text{H}^+ + 6\text{e}^-$	\square 2NH_4^+	-0.28
$\text{NAD}^+ + \text{H}^+ + 2\text{e}^-$	\square NADH	-0.320
$\text{NADP}^+ + \text{H}^+ + 2\text{e}^-$	\square NADPH	-0.324
$2\text{H}^+ + 2\text{e}^-$	\square H_2 (pH 7)	-0.414
$\text{CO}_2 + 4\text{H}^+ + 4\text{e}^-$	\square $1/6$ glucose + H_2O	-0.43
$\text{Fe}^{2+} + 2\text{e}^-$	\square Fe	-0.85

Appendix: Determining oxidized/reduced forms using oxidation state.

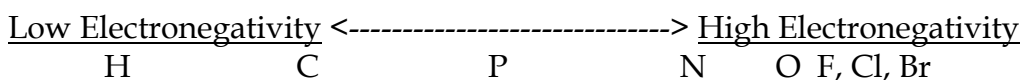
If the molecule is not listed in a table, you must look at the structure to determine the oxidation state of the atoms involved.

- an atom whose oxidation state **decreases** during a reaction is being **reduced**
- an atom whose oxidation state **increases** during a reaction is being **oxidized**

Typically, in any given reaction, only one atom in a given molecule will be oxidized or reduced. Therefore, it is safe to consider the oxidation state only of those atoms that are in different configurations in the two forms of the molecule.

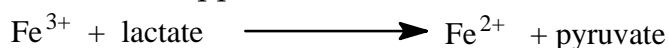
Oxidation state is defined as, "the charge that an atom in a substance would have if the pairs of electrons in each bond belonged to the more electronegative atom".

Electronegativity is the tendency of an atom to hold on to its electrons. The relative electronegativities of atoms found in biological molecules are shown below:



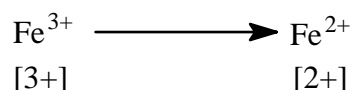
Atoms in their elemental state (H₂, O₂, etc.) have an oxidation state of 0.

These rules can be applied to the reaction below:



For the Fe²⁺ and Fe³⁺, figuring the oxidation state is easy. Since it isn't bonded to anything, its oxidation state is equal to its charge. The number in brackets [X] is the oxidation state.

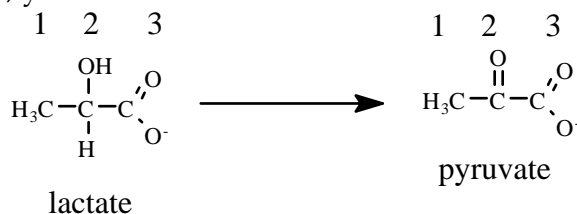
So the Fe half reaction becomes:



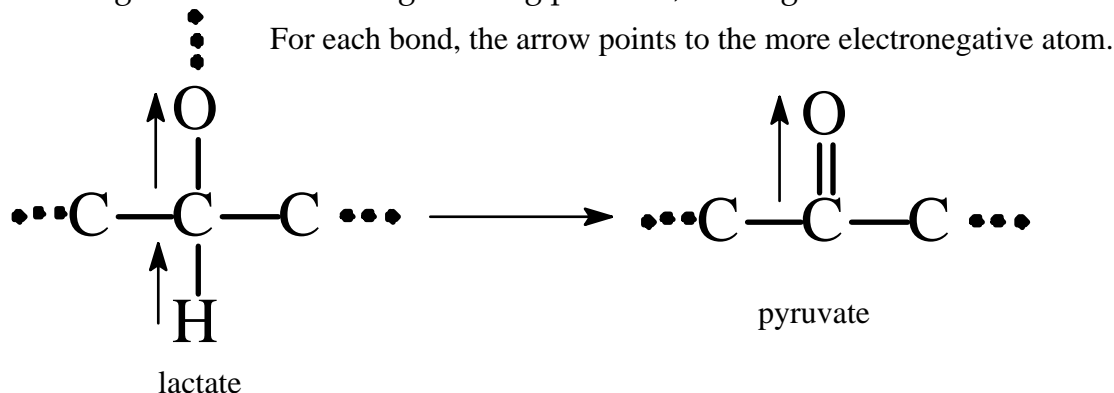
Since the oxidation state of the Fe³⁺ decreases, it is being reduced (gains e⁻).

At this point, the problem is solved. Since Fe³⁺ is being reduced, lactate is being oxidized (redox reactions always occur in oxidation/reduction pairs). But just to be sure, check the change in oxidation state of the lactate as it is converted to pyruvate.

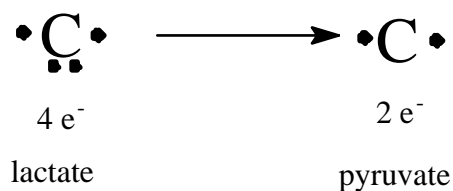
For this, you must look at the chemical structures of lactate and pyruvate:



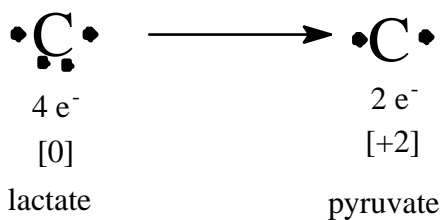
Since the structure of carbons 1 and 3 are not changed in this reaction, we can ignore them when looking for the redox changes taking place. So, looking at carbon 2:



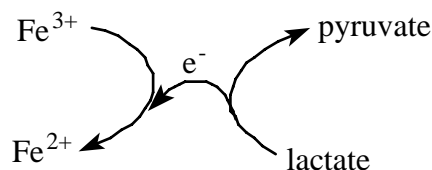
The next step is to assign the electrons in a bond to the more electronegative atom. Note that since carbon has the same electronegativity as carbon, the electrons in a C-C bond are split equally between the two atoms. Since only the middle carbon changes state, it is all we have to look at:



Since carbon is a group IV element, it normally has 4 e⁻. Any fewer e⁻ and it will have a (+) oxidation state, any more and it will have a (-) oxidation state. This gives:



Therefore, since the oxidation state of carbon (2) in lactate increases, it is being oxidized. This gives:



Therefore:

- lactate is oxidized to pyruvate
- Fe³⁺ is reduced to Fe²⁺
- Fe³⁺ is the oxidizing agent
- lactate is the reducing agent
- lactate and Fe²⁺ are the reduced forms
- pyruvate and Fe³⁺ are the oxidized forms

