<u>Redox Chemistry Review</u>

I. Oxidation State or Number

The **oxidation state** or number of a compound gives a *relative* measure of how **oxidized** (electron-poor) or **reduced** (electron-rich) a compound is. The number is relative because it is only meaningful when compared to the number for another compound, to determine which one is more oxidized or more reduced.

Rules for calculating the oxidation state of an element in a molecule (from Brock, *Biology of Microorganisms*, 11^{th} Ed. Appendix A-1).

1. The oxidation state of an element in an elementary substance (*e.g.*, H_2, O_2) is zero.
2. The oxidation state of the ion of an element is equal to its charge (*e.g.*, $Na^+ = +1$, $O^{2-} = -2$).
3. The sum of the oxidation numbers of all atoms in a neutral molecule is zero. Thus, H_2O is neutral because it has two H at +1 each and one O at –2.
4. In an ion, the sum of the oxidation numbers of all atoms is equal to the charge on that ion. Thus, in the OH^- ion, O(-2) + H(+1) = -1
5. In compounds, the oxidation state of O is virtually always –2, and that of H is +1 (this gets more complicated in some organic compounds).
6. In simple carbon compounds, the oxidation state of C can be calculated by adding up the H and O atoms present and using the oxidation states of these elements as given in #5, because in a neutral compound, the sum of the oxidation numbers must be 0. Thus, the oxidation state of carbon in methane, CH_4, is –4 (4 H at +1 = +4).
7. In organic compounds with more than one C atom, it may not be possible to assign a specific oxidation number to each C atom, but it is still useful to calculate the oxidation state of the compound as a whole. Thus, the oxidation state of carbon in glucose, $C_6H_{12}O_6$, is zero and the oxidation state of carbon in ethanol, C_2H_6O, is –2.

i. Calculate the oxidation state of each element in the following compounds (answers at end).

A. sulfate – SO_4^{2-} S: ___________ B. hydrogen sulfide – H_2S S: ___________

C. ammonia – NH_3 N: ___________ D. nitrite – NO_2^- N: ___________

E. nitrate – NO_3^- N: ___________ F. CO_2 C: ___________

G. iron hydroxide – $Fe(OH)_3$ Fe: ___________

II. Reduction and oxidation reactions

The oxidation states you just calculated above provide information about how **reduced** (electron-rich) or **oxidized** (electron-poor) each element in a compound is. The smaller (more negative) the oxidation state, the more reduced a compound is; conversely, larger (more positive) oxidation states are associated with more oxidized compounds. Hence, Fe^{3+} (oxidation state +3) is more oxidized than elemental Fe (oxidation state 0).

Reduction and oxidation reactions (together known as **redox**) involve the transfer of electrons (e^-) from one molecule to another. Since free electrons cannot exist in solution, these reactions are always coupled. Generally, electrons are transferred from more reduced compounds to more oxidized compounds, since the reduced compounds are more electron rich than oxidized compounds. The process of losing electrons is called **oxidation** and the process of gaining electrons is called **reduction**.

A helpful mnemonic: "LEO the lion says GER." (**L**oss of **E**lectrons is **O**xidation;
Gain of **E**lectrons is **R**eduction).

In a redox reaction, the **oxidizing agent** is the reactant that gains electrons and is therefore reduced through the reaction (causing the other compound to become more oxidized). Conversely, the **reducing agent** is the compound that loses electrons through the reaction and therefore is oxidized through the reaction (causing the other compound to become more reduced).

There are different ways of writing redox reactions. Let's use the example of acetaldehyde (CH_3CHO) getting reduced to ethanol (CH_3CH_2OH), a process that happens in respiration, using NADH as the electron source. NADH is common biological molecule that is frequently the source of reducing power. In its oxidized form, NAD^+, it is a common electron acceptor.

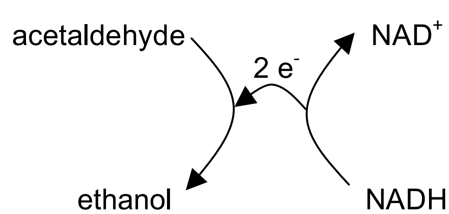
1. Sum of two half reactions:

$$\text{acetaldehyde} + 2\,H^+ + 2\,e^- \longrightarrow \text{ethanol}$$

$$\text{NADH} \longrightarrow NAD^+ + H^+ + 2\,e^-$$

$$\text{acetaldehyde} + H^+ + \text{NADH} \longrightarrow \text{ethanol} + NAD^+$$

2. Electron-transfer diagram:



3. Overall reaction (doesn't show electrons):

$$\text{acetaldehyde} + H^+ + \text{NADH} \longrightarrow \text{ethanol} + NAD^+$$

ii. Fill in the blanks.

A. Through this redox reaction, ________________ is oxidized to ________________.

B. ________________ is reduced to ________________.

C. ________________ is the oxidizing agent and ________________ is the reducing agent.

D. ________________ and ________________ are the oxidized forms.

E. ________________ and ________________ are the reduced forms.

Given an overall reaction, how do we know which reactant is the oxidizing agent and which one is the reducing agent?

For simple compounds, we can use the oxidation states with the general rules in Part I.

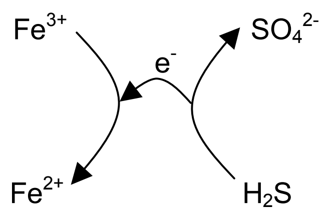
$$\textit{e.g.}\ H_2S + 4\,H_2O + 8\,Fe^{3+} \longrightarrow 8\,Fe^{2+} + 10\,H^{+} + SO_4^{2-}$$

Question: Is the S or the Fe getting reduced or oxidized?

Oxidation number of S: $H_2S = -2$, $SO_4^{2-} = +6$
Oxidation number of Fe: $Fe^{3+} = +3$, $Fe^{2+} = +2$

Since the oxidation number for S increases, the sulfur is getting oxidized.
Since the oxidation number for Fe decreases, the iron is getting reduced.

In an electron-transfer diagram, we would draw this reaction this way:



However, it is not always this easy to determine the oxidizing and reducing agents. Fortunately, there are tables showing the half-reactions for many common reduction reactions, such as the one at the end of this handout. Let's use the following reaction from the citric acid cycle ($FADH_2$ is a compound similar to NADH):

$$\text{succinate} + \text{FAD} \longrightarrow \text{fumarate} + FADH_2$$

From Table 1, we can obtain the following 2 half-reactions (don't worry about $E_0'(V)$ yet):

(1) $\text{fumarate} + 2\,H^{+} + 2\,e^{-} \longrightarrow \text{succinate}$

(2) $\text{FAD} + 2\,H^{+} + 2\,e^{-} \longrightarrow FADH_2$

We have to reverse equation (2) to get the reactant on the correct side. If the number of electrons is not the same in both reactions, multiply one or both reactions by the appropriate number so that the e^- will cancel when the two equations are added together. Remember, overall equations don't show e^-.

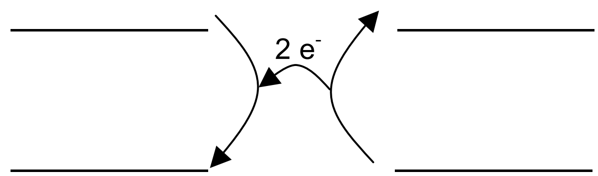
$$\text{succinate} \longrightarrow \text{fumarate} + 2\,H^+ + 2\,e^-$$

$$\text{FAD} + 2\,H^+ + 2\,e^- \longrightarrow \text{FADH}_2$$

$$\text{succinate} + \text{FAD} \longrightarrow \text{fumarate} + \text{FADH}_2$$

iii. Fill in the blanks.

A.



B. ________________ is the oxidizing agent.

C. ________________ is the reducing agent.

III. Redox reactions and thermodynamics

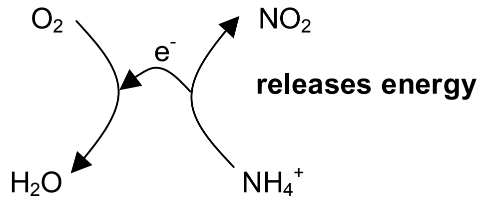
Will the reaction of succinate and FAD occur spontaneously (**exothermic reaction**) or will it require energy input (**endothermic reaction**)? We can use thermodynamics to answer this question. Different molecules have different tendencies to donate or accept e^-. The compounds in Table 1 are ranked according to their tendency to be in the oxidized form (on the left) or in the reduced form (on the right). Generally speaking, the more reduced a molecule is, the more potential energy it contains that can be released for biological work.

Table 1 contains values for E_0', which is **reduction potential**. Reduction potential is a measure of how likely the reduction (forward) reaction is to occur. When comparing two reactions, the one with a higher reduction potential (more positive, *i.e.*, higher in the table) is more likely to occur in the forward direction. Essentially, electrons will move up the table, flowing from the reduced compound in the reaction with the lower reduction potential to the oxidized compound in the reaction with the higher reduction potential.

Take any two equations. The reactant on the left side of the higher equation will be the oxidizing agent, and accept electrons from the product of the lower equation, which will be the reducing agent (by donating electrons). Generally, oxidized compounds higher in the chart are stronger oxidizing agents than the oxidized compounds lower in the chart. Conversely, the reduced compounds lower in the chart are stronger reducing agents than those higher in the chart.

Let's take an example:		E_0'(V)
(1)	$\frac{1}{2}\,O_2 + 2\,H^+ + 2\,e^- \longrightarrow H_2O$	+0.816
(2)	$NO_2^- + 8\,H^+ + 6\,e^- \longrightarrow NH_4^+ + 2\,H_2O$	+0.34

In this system, since the E_0' value is greater for reaction (1), reaction (1) will proceed forwards and reaction (2) will proceed backwards. In other words, O_2 is a stronger oxidizing agent than NO_2^-, so NH_4^+ will be oxidized to NO_2^-, and O_2 will be reduced to H_2O.



This reaction will occur spontaneously and release energy because it is thermodynamically favorable. The measure of this is **$\Delta G^{0'}$**, or the **Gibbs free energy**.

When **$\Delta G^{0'} < 0$**, energy is released and reactions proceed without added energy. (Think of sledding down a hill).
When **$\Delta G^{0'} > 0$**, energy is required to make a reaction proceed. (Think of pushing a sled uphill).

It is possible for NO_2^- to oxidize H_2O to O_2, but this would require additional energy.

Reduction potential values can be used to calculate $\Delta G^{0'}$ according to the **Nernst Equation:**

$$\Delta G^{0'} = -n\mathcal{F}(\Delta E_0')$$

n = number of e^- transferred
$\mathcal{F}$ = Faraday constant (23 kcal V^{-1} mol^{-1})
$\Delta E_0'$ = E_0'(oxidizing agent) - E_0'(reducing agent)

$\Delta E_0'$ and $\Delta G^{0'}$ have opposite signs, so when $\Delta E_0' > 0$, then $\Delta G^{0'}$ will be negative.

Using NH_4^+/O_2 example, let's calculate $\Delta E_0'$ and $\Delta G^{0'}$.

$$3/2\ O_2 + 6\ H^+ + 6\ e^- \longrightarrow 3\ H_2O \qquad E_0' = +0.816\ V\ ^*$$

$$NH_4^+ + 2\ H_2O \longrightarrow NO_2^- + 8\ H^+ + 6\ e^- \qquad E_0' = -0.34\ V\ ^{**}$$

$$NH_4^+ + 3/2\ O_2 \longrightarrow NO_2^- + 2\ H^+ + H_2O \qquad \Delta E_0' = +0.476\ V$$

$$\Delta G^{0'} = -(6)*(23\ kcal\ V^{-1}\ mol^{-1})*(0.476\ V) = -65.688\ kcal/mol$$

Note: *Multiplying by a constant to get the right number of e^- doesn't change $\Delta E_0'$.
**When we reversed reaction (2), we had to change the sign on $\Delta E_0'$.

iv. Going back to the succinate and FAD example, calculate $\Delta E_0^{'}$ and $\Delta G^{0'}$. Will this reaction occur spontaneously?

v. For an overall reaction with CO_2 and H_2S as reactants and H_2O, S and 1 mole of glucose as products, calculate $\Delta E_0^{'}$ and $\Delta G^{0'}$. Will this reaction occur spontaneously?

Final notes:

This is highly over-simplified. For a more complete description, please consult a thermodynamics or chemistry book.

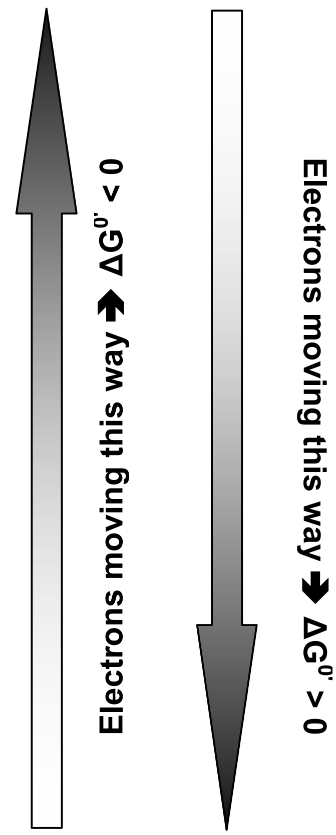
All of these reactions are affected by pH and concentrations of products and reactants. Furthermore, some products or reactants can be further stabilized by other chemical reactions (*e.g.*, Fe^{3+} can precipitate as $Fe(OH)_3$), which also alter the equilibrium.

Thermodynamics describes a world at steady state, but our world is not at thermodynamic equilibrium. Kinetics, or the rates of reactions, also determines whether a reaction will occur or not. Thermodynamics would predict the oxidation of all carbon on earth to CO_2, since O_2 is such a strong oxidant (notice its place in Table 1). However, conversion of solar energy into reduced carbon compounds by autotrophs leads to higher energy configurations and means that thermodynamically unstable configurations (such as our bodies) can occur.

Table 1. Standard reduction potential ($E_0^{'}$) values (at 25^{o}C and pH 7)

Since e^- are being added to the reactants on the left sides of the equations, these reactions are showing **reduction** reactions.

Half-Reaction			$E_o^{'}$ (V)
½ $O_2 + 2 H^+ + 2 e^-$	⇒	H_2O	+0.816
$Fe^{3+} + e^-$	⇒	Fe^{2+}	+0.771
$NO_3^- + 6 H^+ + 6 e^-$	⇒	½ $N_2 + 3 H_2O$	+0.75
$NO_3^- + 2 H^+ + 2 e^-$	⇒	$NO_2^- + H_2O$	+0.421
$NO_3^- + 10 H^+ + 8 e^-$	⇒	$NH_4^+ + 3 H_2O$	+0.36
$NO_2^- + 8 H^+ + 6 e^-$	⇒	$NH_4^+ + 2 H_2O$	+0.34
$CH_3OH + 2 H^+ + 2 e^-$	⇒	$CH_4 + H_2O$	+0.17
fumarate + $2 H^+ + 2 e^-$	⇒	succinate	+0.031
$2 H^+ + 2 e^-$	⇒	H_2 (pH 0)	+0.00
oxaloacetate + $2 H^+ + 2 e^-$	⇒	malate	-0.166
$CH_2O + 2 H^+ + 2 e^-$	⇒	CH_3OH	-0.18
pyruvate + $2 H^+ + 2 e^-$	⇒	lactate	-0.185
acetaldehyde + $2 H^+ + 2 e^-$	⇒	ethanol	-0.197
$SO_4^{2-} + 8 H^+ + 6 e^-$	⇒	$S + 4 H_2O$	-0.20
$SO_4^{2-} + 10 H^+ + 8 e^-$	⇒	$H_2S + 4 H_2O$	-0.21
$FAD + 2 H^+ + 2 e^-$	⇒	$FADH_2$	-0.219
$CO_2 + 8 H^+ + 8 e^-$	⇒	$CH_4 + 2 H_2O$	-0.24
$S + 2 H^+ + 2 e^-$	⇒	H_2S	-0.243
$N_2 + 8 H^+ + 6 e^-$	⇒	$2 NH_4^+$	-0.28
$NAD^+ + H^+ + 2 e^-$	⇒	NADH	-0.320
$NADP^+ + H^+ + 2 e^-$	⇒	NADPH	-0.324
$2 H^+ + 2 e^-$	⇒	H_2 (pH 7)	-0.414
$CO_2 + 4 H^+ + 4 e^-$	⇒	1/6 glucose + H_2O	-0.43
$Fe^{2+} + 2 e^-$	⇒	Fe	-0.85

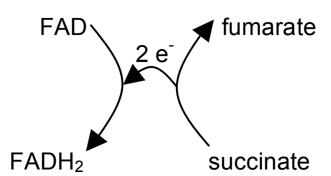


Answers to sample problems.

i. A. S: +6 B. S: -2 C. N: -3 D. N: +3
E. N: +5 F. C: +4 G. Fe: +3

ii. A NADH is oxidized to NAD^+
B. Acetaldehyde is reduced to ethanol
C. Acetaldehyde is the oxidizing agent and NADH is the reducing agent.
D. Acetaldehyde and NAD^+ are the oxidized forms.
E. Ethanol and NADH are the reduced forms.

iii. A.



B. FAD is the oxidizing agent.

C. Succinate is the reducing agent.

iv. $\Delta E_0^{'} = -0.250$ V; $\Delta G^{0'} = +11.5$ kcal/mol; No.

v. $\Delta E_0^{'} = -0.187$ V; $\Delta G^{0'} = +103.2$ kcal/mol; No. This reaction describes the production of glucose, a process that we know requires a considerable amount of energy. Since this reaction is a photosynthetic reaction, this necessary energy is provided by sunlight.

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