therefore gain 2 electrons to balance charges, one for B^+ and a second for the additional H^+ that was added. Together this information leads you to conclude that the most likely thing to have happened is that two electrons were exchanged between **AH** and **B$^+$**.

- This will also be the case for most redox reactions in biology. Fortunately, in most cases, either the context of the reaction, the presence of chemical groups often engaged in redox (e.g. metal ions), or the presence of commonly used electron carriers (e.g. $NAD^+/NADH$, $FAD^+/FADH_2$, ferredoxin, etc.) will alert you that the reaction is of class "redox". You will be expected to learn to recognize some of these common molecules.

Reduction Potential

By convention, we quantitatively characterize redox reactions using an measure called **reduction potentials.** The reduction potential attempts to quantitatively describe the "ability" of a compound or molecule to gain or lose electrons. The specific value of the reduction potential is determined experimentally, but for the purpose of this course we assume that the reader will accept that the values in provided tables are reasonably correct. We can anthropomorphize the reduction potential by saying that it is related to the strength with which a compound can "attract" or "pull" or "capture" electrons. Not surprisingly this is is related to but not identical to electronegativity.

What is this intrinsic property to attract electrons?

Different compounds, based on their structure and atomic composition have intrinsic and distinct "attractions" for electrons. This quality leads each molecule to have its own standard **reduction potential** or **$E^{0'}$**. The reduction potential is a relative quantity (relative to some "**standard**" reaction). If a test compound has a stronger "attraction" to electrons than the standard (if the two competed, the test compound would "take" electrons from the standard compound), we say that the test compound has a positive reduction potential. The magnitude of the difference in E_0' between any two compounds (including the standard) is proportional to how much more or less the compounds "want" electrons. The relative strength of the reduction potential is measured and reported in units of **Volts (V)** (sometimes written as electron volts or eV) or **milliVolts (mV)**. The reference compound in most redox towers is H_2.

Possible NB Discussion Point

Rephrase for yourself: How do you describe or think about the difference between the concept of electronegativity and red/ox potential?

Redox student misconception alert: The standard redox potential for a compound reports how strongly a substance wants to hold onto an electron in comparison to hydrogen. Since both redox potential and electronegativity are both discussed as measurements for how strongly something "wants" an electron, they are sometimes conflated or confused for one another. However, they are not the same. While the electronegativity of atoms in a molecule may influence its redox potential, it is not the only factor that does. You don't need to worry about how this works. For now, try to keep them as different and distinct ideas in your mind. The physical relationship between these two concepts is well beyond the scope of this general biology class.

REQUEST

As you go through the Redox section of the reading please use NB to also comment on parts of the reading that are hard to understand, confusing, and places that you think are well explained and clear. If you have suggested edits please let us know. Use the following emoji to tag these comments:

🛠️

Table of Standard Reduction Potentials (aka. The Redox Tower)

All kinds of compounds can take part in redox reactions. Scientists have developed a graphical tool, a table of standard reduction potentials (aka. a redox tower), to tabulate redox half reactions based on their $E^{0'}$ values. This tool can help predict the direction of electron flow between potential electron donors and acceptors and how much free energy change might be expected to change in a specific reaction. By convention, all half reactions in the table are written in the direction of reduction for each compound listed.

In the biology context, the redox tower usually ranks a variety of common compounds (their half reactions) from most negative $E^{0'}$ (compounds that readily get rid of electrons), to the most positive $E^{0'}$ (compounds most likely to accept electrons). The tower below lists the number of electrons that are transferred in each reaction. For example, the reduction of NAD^+ to NADH involves two electrons, written in the table as $2e^-$.

oxidized form	reduced form	n (electrons)	$E^{0'}$ (volts)
PS1* (ox)	PS1* (red)	-	-1.20
Acetate + CO_2	pyruvate	2	-0.7
ferredoxin (ox) *version 1*	ferredoxin (red) *version 1*	1	-0.7

oxidized form	reduced form	n (electrons)	$E^{0'}$ (volts)
succinate + CO_2 + $2H^+$	a-ketoglutarate + H_2O	2	-0.67
PSII* (ox)	PSII* (red)	-	-0.67
P840* (ox)	PS840* (red)	-	-0.67
acetate	acetaldehyde	2	-0.6
glycerate-3-P	glyceraldehyde-3-P + H_2O	2	-0.55
O_2	O_2^-	1	-0.45
ferredoxin (ox) *version 2*	ferredoxin (red) *version 2*	1	-0.43
CO_2	glucose	24	-0.43
CO_2	formate	2	-0.42
2H+	H_2	2	-0.42 (at $[H^+]$ = 10^{-7}; pH=7) Note: at $[H^+]$ = 1; pH=0, the $E^{0'}$ for hydrogen is ZERO. You will see this in chemistry class.
α-ketoglutarate + $CO_2 + 2H^+$	isocitrate	2	-0.38
acetoacetate	b-hydroxybutyrate	2	-0.35
Cystine	cysteine	2	-0.34
Pyruvate + CO_2	malate	2	-0.33
$NAD^+ + 2H^+$	NADH + H^+	2	-0.32
$NADP^+ + 2H^+$	NADPH + H^+	2	-0.32

oxidized form	reduced form	n (electrons)	$E^{0'}$ (volts)
Complex I FMN (enzyme bound)	$FMNH_2$	2	-0.3
Lipoic acid, (ox)	Lipoic acid, (red)	2	-0.29
1,3 bisphosphoglycerate + $2H^+$	glyceraldehyde-3-P + P_i	2	-0.29
Glutathione, (ox)	Glutathione, (red)	2	-0.23
FAD^+ (free) + $2H^+$	$FADH_2$	2	-0.22
Acetaldehyde + $2H^+$	ethanol	2	-0.2
Pyruvate + $2H^+$	lactate	2	-0.19
Oxalacetate + $2H^+$	malate	2	-0.17
α-ketoglutarate + NH_4+	glutamate	2	-0.14
FAD^+ + $2H^+$ (bound)	$FADH_2$ (bound)	2	0.003-0.09
Methylene blue, (ox)	Methylene blue, (red)	2	0.01
Fumarate + $2H^+$	succinate	2	0.03
CoQ (Ubiquinone - UQ + H^+)	UQH**.**	1	0.031
UQ + $2H^+$	UQH_2	2	0.06
Dehydroascorbic acid	ascorbic acid	2	0.06
Plastoquinone; (ox)	Plastoquinone; (red)	-	0.08
Ubiquinone; (ox)	Ubiquinone; (red)	2	0.1

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oxidized form	reduced form	n (electrons)	$E^{0'}$ (volts)
Complex III Cytochrome b_2; Fe^{3+}	Cytochrome b_2; Fe^{2+}	1	0.12
Fe^{3+} (pH = 7)	Fe^{2+} (pH = 7)	1	0.20
Complex III Cytochrome c_1; Fe^{3+}	Cytochrome c_1; Fe^{2+}	1	0.22
Cytochrome c; Fe^{3+}	Cytochrome c; Fe^{2+}	1	0.25
Complex IV Cytochrome a; Fe^{3+}	Cytochrome a; Fe^{2+}	1	0.29
$1/2\ O_2 + H_2O$	H_2O_2	2	0.3
$P840^{GS}$ (ox)	$PS840^{GS}$ (red)	-	0.33
Complex IV Cytochrome a_3; Fe^{3+}	Cytochrome a_3; Fe^{2+}	1	0.35
Ferricyanide	ferrocyanide	2	0.36
Cytochrome f; Fe^{3+}	Cytochrome f; Fe^{2+}	1	0.37
PSI^{GS} (ox)	PSI^{GS} (red)	.	0.37
Nitrate	nitrite	1	0.42
Fe^{3+} (pH = 2)	Fe^{2+} (pH = 2)	1	0.77
$1/2\ O_2 + 2H^+$	H_2O	2	0.816
$PSII^{GS}$ (ox)	$PSII^{GS}$ (red)	-	1.10

* Excited State, after absorbing a photon of light
GS Ground State, state prior to absorbing a photon of light
PS1: Oxygenic photosystem I
P840: Bacterial reaction center containing bacteriochlorophyll (anoxygenic)
PSII: Oxygenic photosystem II

Table 1. *Common redox tower used in Bis2A. By convention the tower half reactions are written with the oxidized form of the compound on the left and the reduced form on the right. Compounds that make good electron donors have highly negative reduction potentials. Compounds such as Glucose and Hydrogen gas are excellent electron donors. By contrast compounds that make excellent electron acceptors, such as Oxygen and Nitrite are excellent electron acceptors.*

Video on redox tower

For a short video on how to use the electron tower in redox problems click here or below. This video was made by Dr. Easlon for Bis2A students. (This is quite informative.)

What is the relationship between $\Delta E^{0'}$ and $\Delta G^{0'}$?

How do we know if any given redox reaction (the specific combination of two half reactions) is energetically spontaneous or not (exergonic or endergonic)? Moreover, how can we determine what the quantitative change in free energy is for a specific redox reaction? The answer lies in the difference in the reduction potentials of the two compounds. The difference in the reduction potential for the reaction ($\mathbf{\Delta E^{0'}}$), can be calculated by taking the difference between the $E^{0'}$ for the **oxidant** (the compound getting the electrons and causing the oxidation of the other compound) and the **reductant** (the compound losing the electrons). In our generic example below, AH is the reductant and B^+ is the oxidant. Electrons are moving from AH to B^+. Using the $E^{0'}$ of -0.32 for the reductant and +0.82 for the oxidant the total change in $E^{0'}$ or $\mathbf{\Delta E^{0'}}$ is 1.14 eV.

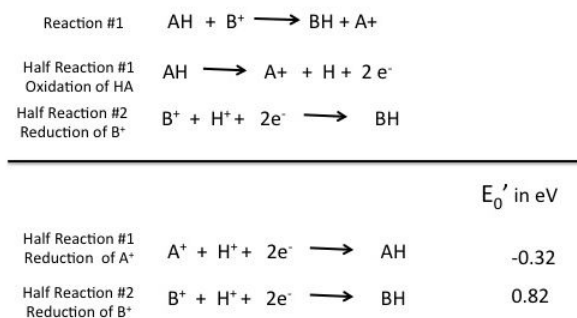|			E_0' in eV
Reaction #1	AH + B⁺ ⟶ BH + A+		
Half Reaction #1 Oxidation of HA	AH ⟶ A+ + H + 2 e⁻		
Half Reaction #2 Reduction of B⁺	B⁺ + H⁺+ 2e⁻ ⟶ BH		
Half Reaction #1 Reduction of A⁺	A⁺ + H⁺+ 2e⁻ ⟶ AH	-0.32	
Half Reaction #2 Reduction of B⁺	B⁺ + H⁺+ 2e⁻ ⟶ BH	0.82	

Figure 4. *Generic red/ox reaction with half reactions written with reduction potential ($E^{0'}$) of the two half reactions indicated.*

$\Delta E^{0'}$ between oxidant and reductant can tell us about the spontaneity of a proposed electron transfer. Intuitively, if electrons are proposed to move from a compound that "wants" electrons <u>less</u> to a compound that "wants" electrons <u>more</u> (i.e. a move <u>from</u> a compound with a lower $E^{0'}$ <u>to</u> a compound with a higher $E^{0'}$, the reaction will be energetically spontaneous). If the electrons are proposed to move from a compound that "wants" electrons more to a compound that "wants" electrons less (i.e. a move <u>from</u> a compound with a higher $E^{0'}$ <u>to</u> a compound with a lower $E^{0'}$, the reaction will be energetically non-spontaneous). Because of the way biological/biochemical redox tables are ordered (small $E^{0'}$ on top and larger $E^{0'}$ on the bottom) transfers of electrons from donors higher on the table to acceptors lower on the table will be spontaneous.

It is also possible to quantify the amount of free energy change associated with a specific redox reaction. The relationship is given by the following equation:

$$\Delta G^{\circ'} = -n F \Delta E^{\circ'}$$

Figure 5. *The relationship between free energy of a redox reaction to the difference in reduction potential between the reduced products of the reaction and oxidized reactant. Attribution: Marc T. Facciotti*

Where:

- n is the number of moles of electrons transferred
- F is the Faraday constant of 96.485 kJ/V. Sometimes it is given in units of kcal/V which is 23.062 kcal/V, which is the amount of energy (in kJ or kcal) released when one mole of electrons passes through a potential drop of 1 volt

Note that the signs of $\Delta E^{0'}$ and $\Delta G^{0'}$ are opposite one another. When $\Delta E^{0'}$ is positive, $\Delta G^{0'}$ will be negative. When $\Delta E^{0'}$ is negative, $\Delta G^{0'}$ will be positive.

This reading tries to break down some of the more challenging topics that students encounter when studying redox chemistry in General Biology. This reading is not a substitute for your main reading but rather a complement to it that revisits some of the same topics through a different lens.

Finding $\Delta E_0'$

Students often struggle with finding the ΔE for a given redox reaction. One of the main barriers to developing this skill seems to be associated with developing a picture of the redox reaction itself. From the context of most biological redox reactions it is useful to imagine/picture a redox reaction as a simple exchange of electrons between two molecules, an electron donor and an electron acceptor that accepts electrons from the donor.

An analogy with kiwi fruit: To help build this mental picture we offer an analogy. Two people are standing next to one another. At the start, one person is holding a kiwi fruit in their hand and the second person's hands are empty. In this reaction, person 1 gives the kiwi to person 2. At the end of the reaction, person 2 is holding a kiwi and person 1 is not. We can write this exchange of kiwi fruit in the form of a chemical reaction:

person 1(kiwi) + person 2() <-> person 1() + person 2(kiwi).
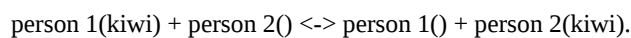
start/initial state <-> final/end state

If we read this "reaction" from left to right, person 1 is a kiwi donor and person 2 is a kiwi acceptor. We can extend this analogy a little by proposing that person 1 and person 2 have different desire and ability to grab and hold kiwi fruit - we'll call that property "kiwi-potential". We can then propose a situation where person 1 and person 2 compete for a kiwi. Let's propose that person 2 has a higher "kiwi-potential" than person 1 - that is, person 2 has a stronger desire and ability to grab and hold kiwi than person 1.

If we set up a competition where person 1 starts with the kiwi and person 2 competes for it, we should expect that after some time the kiwi will be exchanged to person 2 and stay there most often. At the end of the reaction the kiwi will be with person 2. Due to the difference in "kiwi-potential" between person 1 and person 2, we can say that the spontaneous direction of kiwi flow is from person 1 to person 2. If we ever observed the kiwi flow from person 2 to person 1 we could probably conclude that person 1 required some extra help/energy to make that happen - flow from person 2 to person 1 would be non-spontaneous.

Let's call the "kiwi-potential", Kp. In our analogy, $Kp_{person\ 1} < Kp_{person\ 2}$. We can calculate ΔKp, the difference in Kp between the two people, and that will tell us something about how likely we can expect to see kiwi exchange hands between these two people. The

bigger the difference in Kp the more likely the kiwi will move from the person who has a lower Kp to the person who has the higher Kp.

By definition, to calculate ΔKp we obtain the solution to ΔKp = $Kp_{final/end}$ - $Kp_{initial/start}$. Since the kiwi is with person 2 at the end of the reaction and it starts with person 1 at the beginning of the reaction we would calculate ΔKp = $Kp_{person\ 2}$ - $Kp_{person\ 1}$.

Doing it with electrons instead of kiwi fruit: To find $\Delta E^{0'}$ for a redox reaction we can translate this analogy to the molecular space. Instead of people, we have two molecules. Instead of a kiwi, we have electrons. Different molecules have different inherent abilities to grab and hold electrons and this can be measured by the value E. If two molecules exchange one or more electrons we can imagine that electrons will flow spontaneously from a molecule with lower $E^{0'}$ to one with a higher $E^{0'}$. We can write a familiar reaction with those substitutions.

molecule 1(electron) + molecule 2() <-> person 1() + molecule 2(electron).
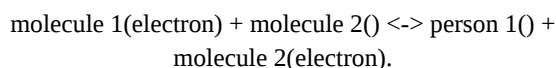
start/initial state <-> final/end state

To find $\Delta E^{0'}$, you solve for $\Delta E^{0'} = E^{0'}_{-final/end}$ - $E^{0'}_{-initial/start}$. Alternatively, you can think of it as $\Delta E^{0'} = E^{0'}_{-acceptor}$ - $E^{0'}_{-donor}$.

When evaluating a redox reaction for $E^{0'}$ you therefore need to:

1. First, find which of the reactants is the electron donor. The donor can also be associated with the initial state because it is the molecule that *initially* (before the start of the reaction) has the electron(s) to donate. This will always be one of the reactants and will be the molecule that gets oxidized (i.e. the molecule that loses electrons).

2. Second, find which of the reactants is the electron acceptor. This will also always be a reactant and will be the molecule that becomes reduced by the reaction (i.e. gains electrons). This molecule can be also associated with the final state since, in its reduced form, it is the molecule that has the electrons at the end of the reaction.

3. Third, calculate $\Delta E^{0'} = E^{0'}_{-acceptor}$ - $E^{0'}_{-donor}$ or if you prefer, $\Delta E^{0'} = E^{0'}_{-final/end}$ - $E^{0'}_{-initial/start}$.

$$NAD^+ + H_2 \longrightarrow NADH + H^+$$
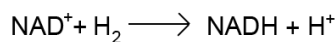
In the example above, we can examine the reactants and determine that NAD^+ is the oxidized form of the electron carrier - it can, therefore, not be the donor. This means that H_2 must act as the electron donor in this reactant. During the reaction electrons flow onto NAD^+ from the donor H_2 creating the reduced product NADH and oxidized product H^+. To calculate $\Delta E^{0'}$ we say that at the start of the reaction the exchanged electrons are on the donor H_2. We say

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that at the end of the reaction the electrons are found on NADH. Calculating $\Delta E^{0'}$ requires us to evaluate the difference:

$E^{0'}$-acceptor - $E^{0'}$-donor

or equivalently,

$E^{0'}$-final/end - $E^{0'}$-initial/start.

Using a redox table to find $E^{0'}$ values for the start and end molecules shows us that $NAD^+/NADH$ has an $E^{0'}$ of -0.30 while H^+/H_2 has an $E^{0'}$ of -0.42.

Therefore, $\Delta E^{0'}$ = (-0.30) - (-0.42) = 0.12 V.

We can see intuitively that this reaction is spontaneous: electrons are flowing from a molecule that "wants" electrons less ($E^{0'}$ of H^+/H_2 = -0.42) to a molecule that wants them more ($E^{0'}$ of $NAD^+/NADH$ = -0.30).

Reading Different Looking Redox Towers

Novice students of redox chemistry will all undoubtedly run across different ways of representing a redox tower. These different representations may look different but contain the same information. Without explanation, however, reading these tables - when they look different - can be confusing. We will compare and contrast different common forms of redox towers.
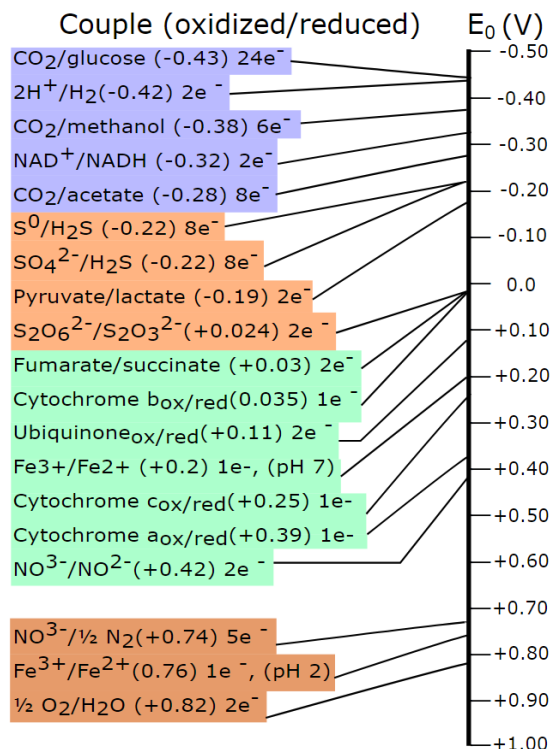
Redox Tower: Type 1

Figure 1. A *Generic redox tower with oxidized/reduced couple listed with its reduction potential ($E^{0'}$). Attribution: Caidon*