REDOX REACTIONS

4TH Semester CC8 TH

Redox reactions (oxidation-reduction) are a form of energy conversion

Redox reactions (oxidation-reduction) are a form of energy conversion involving the transfer of electron pairs from organic substrates to the carrier molecules NAD$^+$

and FAD.

The energy available from redox reactions is due to differences in the electron affinity of two compounds and is an inherent property of each molecule based on molecular structure

Oxidant-Reductant: Half Reactions

Coupled redox reactions consist of two half reactions,

1) an oxidation reaction (loss of electrons)

2) a reduction reaction (gain of electrons)

Compounds that accept electrons are called oxidants and are reduced in the reaction,

whereas compounds that donate electrons are called reductants and are said to be oxidized by loss of electrons

(*Oxidant: An oxidant is a reactant that oxidizes or removes electrons from other reactants during a redox reaction. An oxidant may also be called an oxidizer or oxidizing agent*

***Reductant :a substance capable of bringing about the reduction of another substance as it itself is oxidized*)**

Example

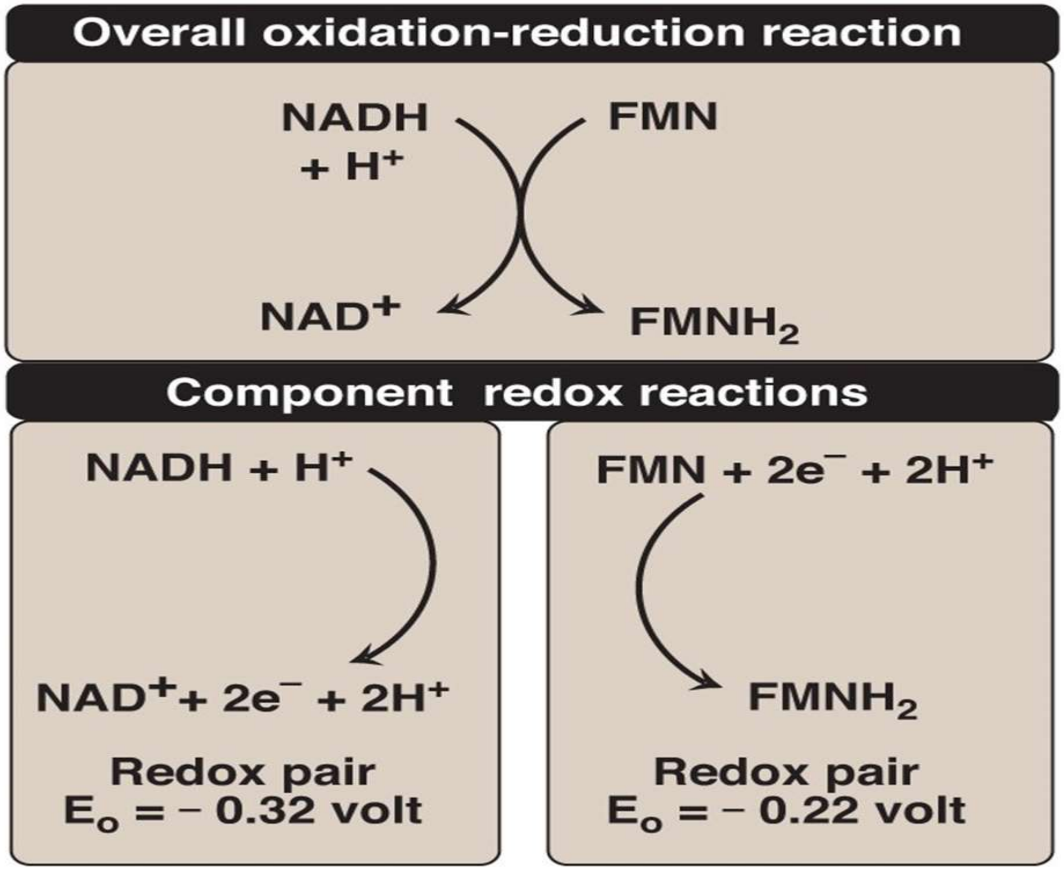
Each half reaction consists of a conjugate redox pair represented by a molecule with and without an electron (e^-). For example, Fe^{2+}/Fe^{3+} is a conjugate redox pair in which the ferrous ion (Fe^{2+}) is the reductant that loses an e^- during oxidation to generate a ferric ion (Fe^{3+}) the oxidant:

Fe^{2+} (reductant) ↔ Fe^{3+} (oxidant) + e

Similarly, the reductant cuprous ion (Cu_+) can be oxidized to form the oxidant cupric ion (Cu_{2+}) plus an e_- in the reaction:

$Cu_{+(reductant)}$ ↔ $Cu_{2+(oxidant)}$ + e

Oxidation of NADH by FMN, separated into two component half-reactions



The two conjugate redox pairs in these reactions are Fe^{2+}/Fe^{3+} and Cu^{+}/Cu^{2+}.

The e^{-} functions as a shared intermediate in the coupled reaction.

$Fe^{2+} \leftrightarrow Fe^{3+}$ + **e-** (oxidation of Fe^{2+})

Cu^{2+} + **e-** ↔ Cu^{+} (reduction of Cu^{2+})

\---

$Fe^{2+} + Cu^{2+} \leftrightarrow Fe^{3+} + Cu^{+}$ (coupled redox reaction)

Glucose to CO_2 and H_2O.

Glucose is fully metabolized by aerobic metabolism to CO_2 and H_2O.

The e^- donor is glucose which functions as the reductant, and O_2 is the e acceptor (oxidant) that is reduced in the last step of the electron transport chain to form H_2O.

The two conjugate redox pairs $NAD^+/NADH$ and $FAD/FADH_2$ serve as the e^- carriers linking glycolysis to the citrate cycle and electron transport chain.

It is useful to think of glucose as a biochemical "battery" containing stored energy in the form of electrons that can be used to synthesize ATP in the mitochondria by oxidative phosphorylation

Electron Carrier 1

Redox reactions in the citrate cycle (and indeed most all enzyme-catalyzed redox reactions) involve the transfer of electron pairs (2 e^-) to the electron carrier molecules NAD^+ and FAD.

The reduction of NAD^+ to NADH involves the
transfer of a hydride ion ($:H^-$), which contains 2 e^- and 1 H^+,
and the release of a proton (H^+) into solution

$$NAD^+ + 2\ e^- + 2\ H^+ \leftrightarrow NADH + H^+$$

Electron carrier 2

In contrast, FAD is reduced by sequential addition of one hydrogen (1 e^- and 1 H^+) at a time to give the fully reduced $FADH_2$ product

$FAD + 1\ e^- + 1\ H^+ \leftrightarrow FADH + 1\ e^- + H^+ \leftrightarrow FADH_2$

Standard Reduction Potential

In redox reactions, we use the term reduction potential (E), measured in volts (V), to represents the electron affinity of a given conjugate redox pair. Analogous to biochemical standard conditions that define Gibbs Free Energy, Gº',

the term Eº' refers to the **biochemical standard reduction potential** under the same conditions.

Eº' values are determined in the laboratory using an apparatus called an electrochemical cell that measures the relative e- affinity of a **test redox pair**, compared to that of the **hydrogen half-reaction** ($2H^+ + 2e^- \leftrightarrow H_2$), which has been chosen as the standard

Release of free energy during electron transport

Standard reduction potential:

The $E^{0`}$ of various redox pairs can be ordered from the most negative to** $E^{0`}$ **the most positive.

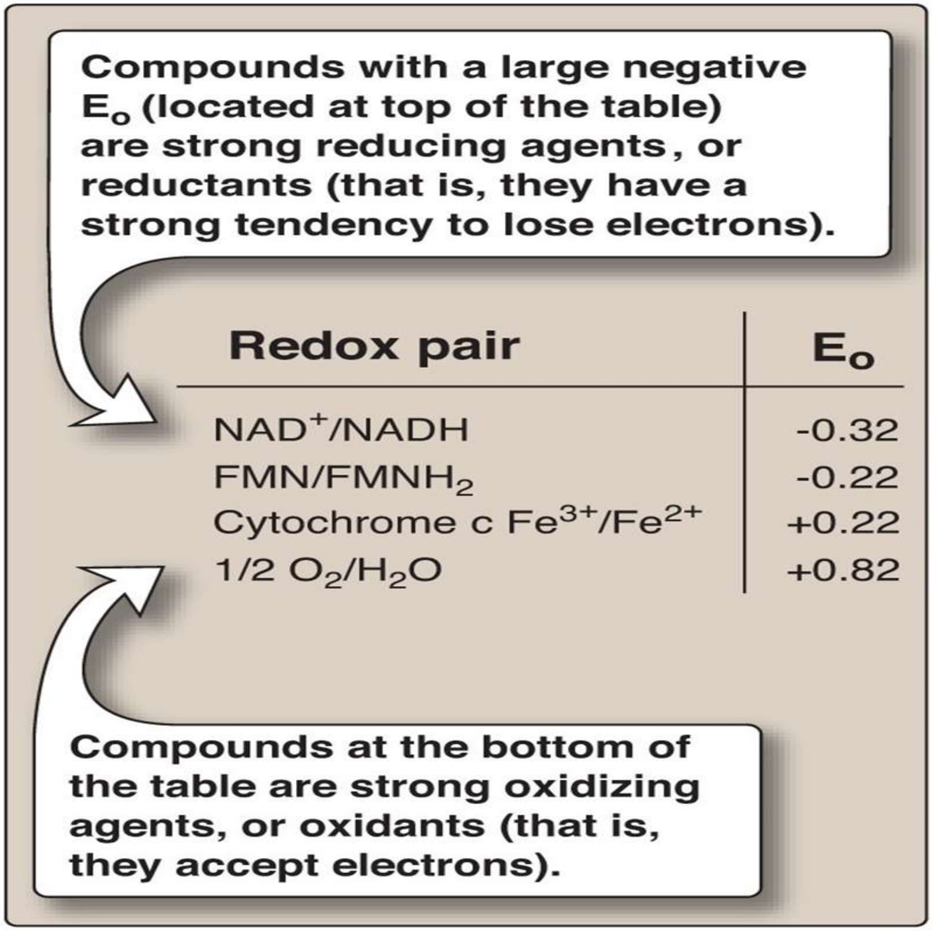
The more negative the $E^{0`}$ of a redox pair, the greater the tendency of the reductant member of that pair to lose electrons.

The more positive the , the greater the tendency of the oxidant member of that pair to accept electrons. Therefore, electrons flow from the pair with the more negative to $E^{0`}$ that with the more positive $E^{0`}$.

The $E^{0`}$ **values for some members of the ETC are shown in Figure**

Note: The components of the chain are arranged in order of increasingly positive $E^{0`}$ values.

Standard reduction potentials (Eo) of some reactions.



Compounds with a large negative E_o (located at top of the table) are strong reducing agents, or reductants (that is, they have a strong tendency to lose electrons).

Redox pair	E_o
$NAD^+/NADH$	-0.32
$FMN/FMNH_2$	-0.22
Cytochrome c Fe^{3+}/Fe^{2+}	+0.22
$1/2\ O_2/H_2O$	+0.82

Compounds at the bottom of the table are strong oxidizing agents, or oxidants (that is, they accept electrons).

Standard reduction potentials of mitochondrial oxidation-reduction components

Substrate or complex	$E^{\circ\prime}$ (V)
NADH	−0.32
Complex I	
FMN	−0.30
Fe—S clusters	−0.25 to −0.05
Succinate	+0.03
Complex II	
FAD	0.0
Fe—S clusters	−0.26 to 0.00
QH_2/Q	+0.04
$(\cdot Q^{\ominus}/Q$	−0.16)
$(QH_2/\cdot Q^{\ominus}$	+0.28)
Complex III	
Fe—S cluster	+0.28
Cytochrome b_{560}	−0.10
Cytochrome b_{566}	+0.05
Cytochrome c_1	+0.22
Cytochrome c	+0.23
Complex IV	
Cytochrome a	+0.21
Cu_A	+0.24
Cytochrome a_3	+0.39
Cu_B	+0.34
O_2	+0.82

Difference between TWO reduction Potential

The amount of energy available from a coupled redox reaction is directly related to the difference between two reduction potentials and is defined by the term ΔEº'.

By convention, the ΔEº' of a coupled redox reaction is determined by subtracting the Eº' of the oxidant (e_- acceptor) from the Eº' of the reductant (e_- donor) using the following equation:

$$\Delta E^{o\prime} = (E^{o\prime}\ e_{-}\ \text{acceptor}) - (E^{o\prime}\ e_{-}\ \text{donor})$$

Relation Between $\Delta E^{o'}$ & $\Delta G^{o'}$

Moreover, the $\Delta E^{o'}$ for a coupled redox reaction is proportional to the change in free energy $\Delta G^{o'}$ as described by the equation:

$\Delta G^{o'} = -nF\Delta E^{o'}$

in which n is the number of electrons transferred in the reaction (usually 2 in biochemical redox reactions), and F is the Faraday constant (96.48 kJ/V•mol).

As can be seen by this equation, when the difference in reduction potentials for a coupled redox reaction is positive then the reaction is favorable since ΔG^{o} will be negative.

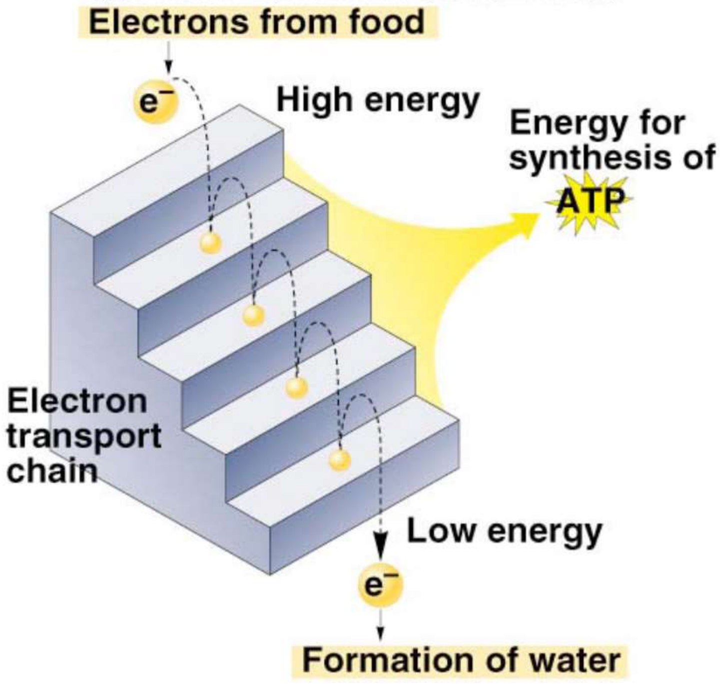
This means that for a coupled redox reaction to be favorable, the reduction potential of the e acceptor needs to be more positive than that of the e_- donor.

Electrons flow downhill

NADH → FMN → Fe-S → Co-Q → (Fe-S / cyt b) → cyt c_1 → cyt c → cyt a → cyt a_3 → O_2

succinate → FAD → Fe-S → Co-Q

- Electrons move in steps from carrier to carrier downhill to O_2
  - each carrier more electronegative
  - controlled oxidation
  - controlled release of energy



The Breakdown of Glucose: An Exergonic Reaction