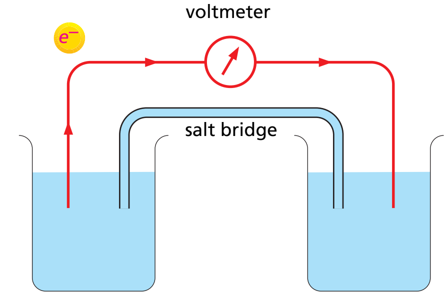
HOW REDOX POTENTIALS ARE MEASURED



$A_{reduced}$ and $A_{oxidized}$ in equimolar amounts

1 M H^+ and 1 atmosphere H_2 gas

One beaker (*left*) contains substance A, with an equimolar mixture of the reduced ($A_{reduced}$) and oxidized ($A_{oxidized}$) members of its redox pair. The other beaker contains the hydrogen reference standard ($2H^+ + 2e^- \rightleftharpoons H_2$), whose redox potential is arbitrarily assigned as zero by international agreement. (A salt bridge formed from a concentrated KCl solution allows the ions K^+ and Cl^- to move between the two beakers, as required to neutralize the charges in each beaker when electrons flow between them.) The metal wire (*red*) provides a resistance-free path for electrons, and a voltmeter then measures the redox potential of substance A. If electrons flow from $A_{reduced}$ to H^+, as indicated here, the redox pair formed by substance A is said to have a negative redox potential. If they instead flow from H_2 to $A_{oxidized}$, the redox pair is said to have a positive redox potential.

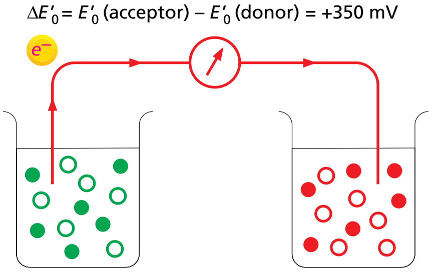
SOME STANDARD REDOX POTENTIALS AT pH7

By convention, the redox potential for a redox pair is designated *E*. For the standard state, with all reactants at a concentration of 1 M, including H^+, one can determine a standard redox potential, designated E_0. Since biological reactions occur at pH 7, biologists use a different standard state in which $A_{reduced} = A_{oxidized}$ and $H^+ = 10^{-7}$ M. This standard redox potential is designated E'_0. A few examples of special relevance to oxidative phosphorylation are given here.

redox reactions	redox potential E'_0
NADH $\rightleftharpoons$ $NAD^+ + H^+ + 2e^-$	–320 mV
reduced ubiquinone $\rightleftharpoons$ oxidized ubiquinone $+ 2H^+ + 2e^-$	+30 mV
reduced cytochrome *c* $\rightleftharpoons$ oxidized cytochrome *c* $+ e^-$	+230 mV
$H_2O \rightleftharpoons \frac{1}{2}O_2 + 2H^+ + 2e^-$	+820 mV

CALCULATION OF $\Delta G°$ FROM REDOX POTENTIALS

$\Delta E'_0 = E'_0$ (acceptor) – E'_0 (donor) = +350 mV



1:1 mixture of NADH and NAD^+

1:1 mixture of oxidized and reduced ubiquinone

$\Delta G° = -8$ kcal/mole

$\Delta G° = -n(0.023)\ \Delta E'_0$, where *n* is the number of electrons transferred across a redox potential change of $\Delta E'_0$ millivolts (mV)

Example: The transfer of one electron from NADH to ubiquinone has a favorable $\Delta G°$ of –8.0 kcal/mole (–1.9 kJ/mole), whereas the transfer of one electron from ubiquinone to oxygen has an even more favorable $\Delta G°$ of –18.2 kcal/mole (–4.35 kJ/mole). The $\Delta G°$ value for the transfer of one electron from NADH to oxygen is the sum of these two values, –26.2 kcal/mole.

THE EFFECT OF CONCENTRATION CHANGES

The actual free-energy change for a reaction, ΔG, depends on the concentration of the reactants and generally is different from the standard free-energy change, $\Delta G°$. The standard redox potentials are for a 1:1 mixture of the redox pair. For example, the standard redox potential of –320 mV is for a 1:1 mixture of NADH and NAD^+. But when there is an excess of NADH over NAD^+, electron transfer from NADH to an electron acceptor becomes more favorable. This is reflected by a more negative redox potential and a more negative ΔG for electron transfer.