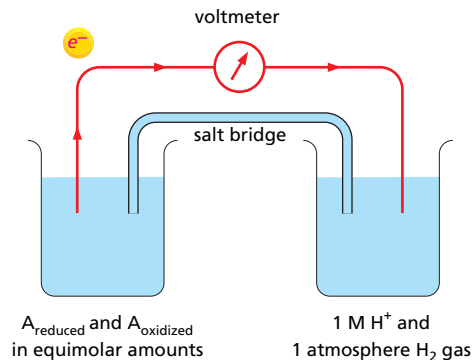


HOW REDOX POTENTIALS ARE MEASURED

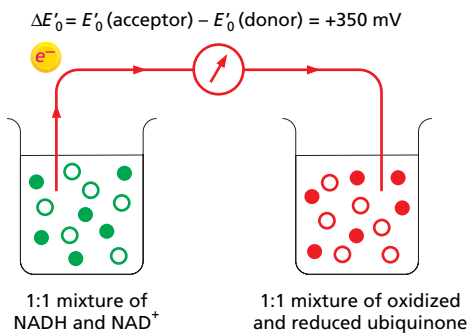


One beaker (*left*) contains substance A, with an equimolar mixture of the reduced (A_{reduced}) and oxidized (A_{oxidized}) members of its redox pair. The other beaker contains the hydrogen reference standard (2H⁺ + 2e⁻ ⇌ H₂), whose redox potential is arbitrarily assigned as zero by international agreement. (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 H₂ 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 ⇌ NAD ⁺ + H ⁺ + 2e ⁻	-320 mV
reduced ubiquinone ⇌ oxidized ubiquinone + 2H ⁺ + 2e ⁻	+30 mV
reduced cytochrome c ⇌ oxidized cytochrome c + e ⁻	+230 mV
H ₂ O ⇌ ½O ₂ + 2H ⁺ + 2e ⁻	+820 mV

CALCULATION OF ΔG° FROM REDOX POTENTIALS

$$\Delta G^\circ = -8 \text{ kcal/mole}$$

$\Delta G^\circ = -n(0.023) \Delta E'_0$, 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 ΔG° of -8.0 kcal/mole (-1.9 kJ/mole), whereas the transfer of one electron from ubiquinone to oxygen has an even more favorable ΔG° of -18.2 kcal/mole (-4.35 kJ/mole). The ΔG° 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, ΔG° . 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.

