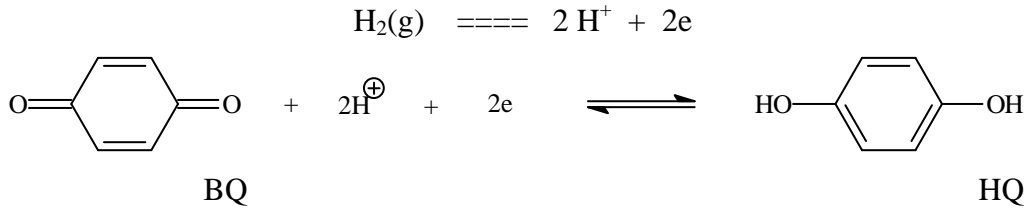


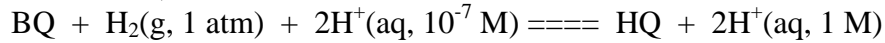
## Environmental Standard Reduction Potentials

We will consider a simple reversible redox reaction for which we are able to measure directly the free energy change,  $\Delta G$ , with a galvanic cell. The redox reaction is the reversible interconversion of 1,4-benzoquinone (BQ) and hydroquinone (HQ) with a platinum electrode immersed in an aqueous solution buffered at pH 7. This half-cell is coupled to a standard hydrogen electrode (SHE), which is an aqueous solution at pH 0 ( $[H^+] = 1 \text{ M}$ ) with  $H_2$  (g) bubbling thru at 1 atm and a platinum electrode. The reactions occurring at each electrode are then:



where we omit the denotation (aq) for dissolved species.

The overall reaction is;



and thus

$$\Delta G = \Delta G^\circ + RT \ln Q = \Delta G^\circ + RT \ln \left( \frac{[HQ][H^+(1M)]^2}{[BQ][H^+(10^{-7}M)]^2 P_{H_2}} \right)$$

and since  $[H^+(1M)] = 1$ , and  $P_{H_2} = 1$ , we obtain

$$\Delta G = \Delta G^\circ + RT \ln \left( \frac{[HQ]}{[BQ] \cdot 10^{-14}} \right)$$

and we can find the cell voltage from:

$$\Delta G = -nFE_H$$

where  $E_H$  is the cell voltage referenced to the SHE.

We can also write:

$$E_H = E_H^\circ - \frac{RT}{nF} \ln \left( \frac{[HQ]}{[BQ] \cdot [H^+]^2} \right)$$

or

$$E_H = E_H^\circ - \frac{0.05916}{n} \log \left( \frac{[HQ]}{[BQ] \cdot [H^+]^2} \right)$$

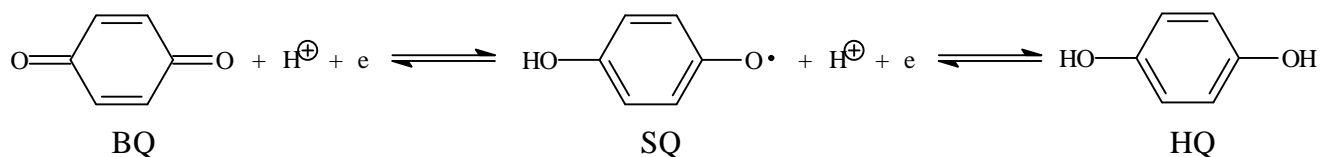
In our example,  $E_H = E_H^\circ$ , if  $[BQ] = [HQ] = [H^+] = 1 \text{ M}$  and for this reaction,  $E_H^\circ$  is +0.70 v at 25°C. However we are dealing with redox reactions occurring in natural waters and are more interested in redox potential values that are more representative of typical natural conditions and not solutions at pH = 0 ( $[H^+] = 1 \text{ M}$ ). We therefore define a  $E_H^\circ(W)$  value

(the W indicating conditions typical for natural waters) by setting the pH = 7,  $[Cl^-] = 10^{-3}$  M for a dechlorination reaction,  $[Br^-] = 10^{-5}$  M for a debromination reaction,  $[HCO_3^-] = 10^{-3}$  M and so on, but by leaving the oxidant and reductant at unit activity.

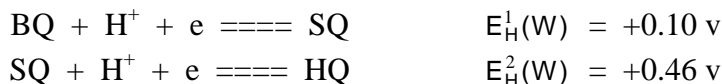
Hence for our reaction;

$$E_H^0(W) = E_H^0 - \frac{0.05916}{n} \log \left( \frac{[HQ]}{[BQ] \cdot [H^+]^2} \right) = 0.70 - \frac{0.05916}{2} \log \left( \frac{1}{1 \cdot (10^{-7})^2} \right) = 0.70 - 14 \times 0.05916 / 2 = 0.28 \text{ v}$$

In this example, we considered a *reversible* redox reaction with an overall transfer of two electrons. Since in most *abiotic* multi-electron redox processes, particularly if organic compounds are involved, the actual electron transfer occurs by a sequence of one-electron transfer steps. There are intermediates formed which are very reactive, that is, they are not stable under environmental conditions. In the example, BQ is first reduced to the corresponding semiquinone (SQ) which is then reduced to HQ:



Each of these subsequent one-electron steps has its own  $E_H^0(W)$  value, which we can denote  $E_H^1(W)$  and  $E_H^2(W)$ :



From these values, we see that the transfer of the first electron to BQ is much less spontaneous (smaller positive voltage), as compared to the transfer of the second electron to SQ. In general, we can assume that the formation of an organic radical is much less favorable from an energetic point of view, as compared to the formation of an organic species exhibiting an even number of electrons. From this we may conclude that the first step of a two-electron transfer between an organic molecule and an electron donor or acceptor is frequently the rate-limiting step. Thus, when we are interested in relating thermodynamic and kinetic data (e.g., thru LFER's), we need to consider primarily the  $E_H$  values of this rate limiting step, that is, the  $E_H$  value of the first one-electron transfer.

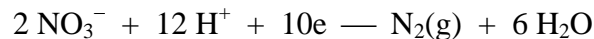
The following table summarizes standard reduction potentials of some environmentally important redox couples.

Standard reduction potentials at 25°C of some redox couples that are important in natural redox processes

	Half-Reaction	$E_H^\circ$ (w) (v)	$E_H^\circ$ (v)	$\Delta G_H^\circ$ (w) / n (kJ.mol <sup>-1</sup> )
1	$O_2(g) + 4 H^+ + 4e \rightarrow 2 H_2O$	+0.81	1.22	-78.3
2	$2 NO_3^- + 12 H^+ + 10e \rightarrow N_2(g) + 6 H_2O$	+0.74	1.24	-71.4
3	$MnO_2(s) + HCO_3^-(10^{-3}M) + 3 H^+ + 2e \rightarrow MnCO_3(s) + 2 H_2O$	+0.52		-50.2
4	$NO_3^- + 2 H^+ + 2e \rightarrow NO_2^- + H_2O$	+0.42	0.83	-40.5
5	$NO_3^- + 10 H^+ + 8e \rightarrow NH_4^+ + 3 H_2O$	+0.36	0.88	-34.7
6	$FeOOH(s) + HCO_3^-(10^{-3}M) + 2 H^+ + e \rightarrow FeCO_3(s) + 2 H_2O$	-0.05		4.6
7	Pyruvate + 2 H <sup>+</sup> + 2e → lactate	-0.19		18.3
8	$SO_4^{2-} + 9 H^+ + 8e \rightarrow HS^- + 4 H_2O$	-0.22	0.25	21.3
9	$S(s) + 2 H^+ + 2e \rightarrow H_2S(g)$	-0.24	0.17	23.5
10	$S(s) + H^+ + 2e \rightarrow HS^-$	-0.27		
11	$CO_2(g) + 2 H^+ + 8e \rightarrow CH_4(g) + 2 H_2O$	-0.25	0.17	23.5
12	$2 H^+ + 2e \rightarrow H_2(g)$	-0.41	0	39.6
13	$6 CO_2(g) + 24 H^+ + 24e \rightarrow C_6H_{12}O_6 + 6 H_2O$	-0.43	-0.01	41.0

Environmental Standard Conditions are taken as;  $[H^+] = 10^{-7} M$ ,  $[Cl^-] = [HCO_3^-] = 10^{-3} M$ ,  $[Br^-] = 10^{-5} M$

It should be pointed out that many of the half-reactions that we consider *do not occur reversibly at an electrode surface, so that we would not be able to measure the corresponding  $E_H$  values using a galvanic cell.* Nevertheless, it is very convenient to express the free energy change of a half-reaction by assigning the appropriate reduction potentials, that is,  $E_H = \Delta G/nF$ . One possibility is to calculate such reduction potentials from thermodynamic data, for example, from standard free energies of formation,  $\Delta G_f^\circ$  of the various species involved in the half-reaction. To illustrate, consider the half-reaction:



which is catalyzed by microorganisms and is commonly referred to as denitrification.

From compilations of  $\Delta G_f^\circ$  values, we calculate  $\Delta G_{rxn}^\circ = \Delta G_H^\circ = -1200.6 \text{ kJ.mol}^{-1}$  (using  $\Delta G_f^\circ(H^+) = \Delta G_f^\circ(e) = 0$ ).

$$E_H^\circ = -\Delta G_H^\circ/nF = +1.24 \text{ v.}$$

The Nernst equation then gives us:

$$E_H = E_H^\circ - \frac{0.05916}{10} \log \left( \frac{[NO_3^-]^2 [H^+]^{12}}{P_{N_2} \cdot [H_2O]^6} \right)$$

With all species except  $H^+$  ( $10^{-7} M$ ) at standard conditions, we obtain

$$E_H^o(W) = E_H^\circ - \frac{0.05916}{10} \log((10^{-7})^{12}) = 1.24 - 0.50 = +0.74 \text{ v}$$

## Redox Processes That Determine Redox Conditions In The Environment

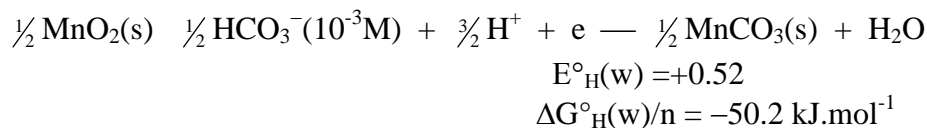
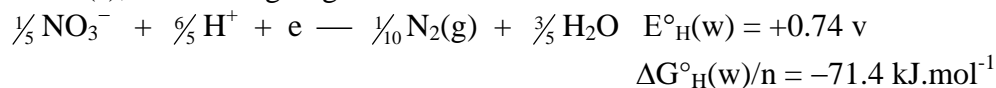
From the data in the table above (Standard Reduction Potentials At 25°C Of Some Redox Couples That Are Important In Natural Redox Processes), we can get a general idea about the maximum free energy that microorganisms may gain from catalyzing redox reactions. On earth, the maintenance of life resulting directly or indirectly from a steady input of solar energy is the main cause for nonequilibrium redox conditions. In the process of photosynthesis, organic compounds exhibiting reduced states of carbon, nitrogen and sulfur are synthesized, and at the same time oxidized species including molecular oxygen, O<sub>2</sub> (oxic photosynthesis) or oxidized sulfur species (anoxic photosynthesis) are produced. Using glucose as a model organic compound, we can express oxic photosynthesis by combining equations (1) and (13) from the above table. Since we are looking at the overall process, it is convenient to write the reaction with a stoichiometry corresponding to the transfer of one electron (remembering that E°<sub>H</sub> and E°<sub>H(w)</sub> are independent of the number of electrons transferred).

	E° <sub>H(w)</sub> (v)	ΔG° <sub>H(w)/n</sub> (kJ.mol <sup>-1</sup> )
From equation (13) above;		
$\frac{1}{4} \text{CO}_2 + \text{H}^+ + \text{e} \longrightarrow \frac{1}{24} \text{C}_6\text{H}_{12}\text{O}_6(\text{glucose}) + \frac{1}{4} \text{H}_2\text{O}$	-0.43	+41.0
We take the reversed form of equation (1) - changing the sign:		
$\frac{1}{2} \text{H}_2\text{O} \longrightarrow \frac{1}{4} \text{O}_2(\text{g}) + \text{H}^+ + \text{e}$	-0.81	+78.3
Overall;		
$\frac{1}{4} \text{CO}_2 + \frac{1}{4} \text{H}_2\text{O} \longrightarrow \frac{1}{24} \text{C}_6\text{H}_{12}\text{O}_6 + \frac{1}{4} \text{O}_2(\text{g})$	-1.24	+119.3

Thus, under standard environmental conditions (pH 7), on a “per electron basis”, an organism utilizes 119.3 kJ.mol<sup>-1</sup> of the sun's energy to photosynthesize glucose from CO<sub>2</sub> and H<sub>2</sub>O. The chemical energy stored in reduced chemical species (including organic pollutants) can now be utilized by organisms that are capable of catalyzing energy yielding redox reactions. For example, we can see from the table above, that in the oxidation of glucose (reversed Reaction 13), oxygen is the most favorable oxidant (i.e., electron acceptor) from an energetic point of view, at least, if O<sub>2</sub> is reduced all the way to H<sub>2</sub>O (which is commonly the case in biologically mediated processes);

	E° <sub>H(w)</sub> (v)	ΔG° <sub>H(w)/n</sub> (kJ.mol <sup>-1</sup> )
$\frac{1}{4} \text{O}_2(\text{g}) + \text{H}^+ + \text{e} \longrightarrow \frac{1}{2} \text{H}_2\text{O}$	+0.81	-78.3
The ΔG° <sub>H(w)/n</sub> value for the reaction of glucose with O <sub>2</sub> (reversed reaction 13 with reaction 1) is:		
$\frac{1}{24} \text{C}_6\text{H}_{12}\text{O}_6 + \frac{1}{4} \text{O}_2(\text{g}) \longrightarrow \frac{1}{4} \text{CO}_2 + \frac{1}{4} \text{H}_2\text{O}$	+1.24	-119.3
and the organism obtains -119.3 kJ.mol <sup>-1</sup> of energy on a “per electron basis”.		

The next “best” electron acceptors would be nitrate,  $\text{NO}_3^-$  (if converted to  $\text{N}_2$ ), then  $\text{MnO}_2(\text{s})$ , and so on going down the list in the table above.



For the reaction of these oxidants with glucose, the organisms would obtain  $-112.4$  and  $-91.2 \text{ kJ}\cdot\text{mol}^{-1}$  respectively on a “per electron basis”. Interestingly, the chemical reaction sequence given in the table above (that is based on standard free energy considerations) is, in essence, paralleled by a spatial and/or temporal succession of different microorganisms in the environment. In other words, in a given (micro)environment, those organisms will be dominant that are capable of utilizing the “strongest” oxidants available (i.e., the electron acceptor with the most positive reduction potential). These microorganisms then in turn determine the redox conditions in that (micro)environment. The figure below illustrates the dynamics of some redox species along the flow path of a contaminant plume in the ground. For simplicity, we assume a situation where we have constant input of reduced (e.g., organic compounds) and oxidized species (e.g.,  $\text{O}_2$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ). Natural or synthetic organic compounds (the major electron donors) are degraded over the whole length of the plume. As long as there is molecular oxygen present, *aerobic (oxic) respiration* takes place, which involves the oxidation of organic compounds by oxygen,  $\text{O}_2$ . Once the oxygen is consumed, *denitrification* is observed until the nitrate is no longer present. In the region where denitrification occurs, one often observes the reductive dissolution of oxidized manganese phases (e.g.,  $\text{MnO}_2(\text{s})$ ,  $\text{MnOOH}(\text{s})$ ). Under these conditions iron is still present in oxidized forms (e.g.,  $\text{FeOOH}(\text{s})$ ). Then, a marked decrease in redox potential occurs when the only electron acceptors left in significant abundance, are those that exhibit low reduction potentials (see table above). This redox sequence has led to a somewhat different terminology in that one speaks of the *oxic* (aerobic), *suboxic* (denitrification, manganese reduction), and *anoxic* conditions (low redox potential). Processes involving electron acceptors (oxidants) exhibiting a low redox potential include, in sequence: *iron reduction*, *sulfate respiration* (or sulfate reduction), and *fermentation* including *methogenesis*. The temporal and/or spatial succession of redox processes as illustrated in the diagram below for the groundwater environment is also observed for other environments in which access to oxygen and other electron acceptors is limited, for example, in sediments of lakes, rivers, and the oceans.

