

Energetics (source, amount, and flow of energy)

Chemical energy is derived from the energy stored in chemical bonds. When bonds are made or broken there is a quantifiable amount of energy expended. This statement holds for both biological and non-biological mediated reactions. Electrons are transferred by oxidation-reduction reactions (redox).

Remember **OIL RIG**

Oxidation **I**s **L**oss of electron
Reduction **I**s **G**ain of electron

Oxidant + e⁻ → reduced form
Reductant - e⁻ → oxidized form

Electron acceptor (gains electrons)
Electron donor (gives up electrons)

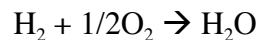
***All redox reactions are coupled half reactions. No free electrons are present. The reactions must be added to make a complete reaction. The generally accepted convention is keep the electrons on the left side of the reaction.

Oxidant + reductant → reduced oxidant + oxidized reductant

Major elements that are redox sensitive under earth surface conditions include: H, O, C, S, N, Fe, and Mn.

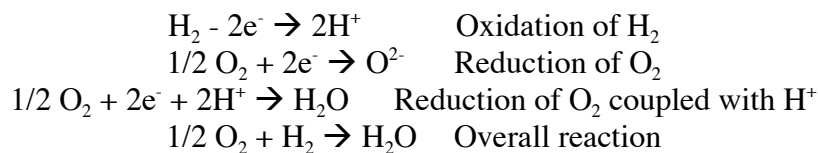
Minor elements that are redox sensitive under earth surface conditions include: V, AS, Se, and Hg

Example of overall redox reaction



H is oxidized (zero state to 1⁺). H is the electron donor (reducing agent or reductant)
O is the reduced (0 to 2⁻). O is the electron acceptor (oxidizing agent or oxidant).

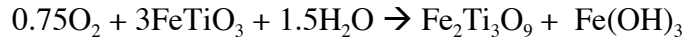
The above reaction is the sum of the following half-reactions



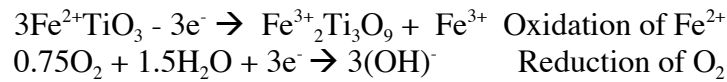
Compounds that serve as either electron acceptor or donors are often expressed as couples with the convention of putting the oxidized form on the left and reduced form on the right, e.g.,

$2\text{H}^+/\text{H}_2$
 $1/2 \text{O}_2 / \text{H}_2\text{O}$
 oxidant/reductant
 acceptor/donor

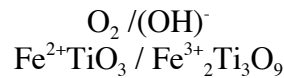
Example of breakdown of ilmenite in soil to pseudorutile



The above reaction is the sum of the following half-reactions



The electron acceptor or donor couples are:



The more stable end product of ilmenite weathering is hematite and anatase/rutile. This is not a redox reaction. It's a dissolution-precipitation reaction.



The transfer of energy during bond-breaking redox reactions is often part of biological processes. Surficial processes are often controlled by microbial and plant mediated reactions (reactions that occur both inside the cell walls and outside the cell walls).

Microbes that gain energy from breaking organic chemical bonds are called **organtrophs**.

Microbes that gain energy from breaking inorganic chemical bonds are called **lithotrophs**.

Microbes that gain energy from sunlight are called **phototrophs**.

The energy (i.e., the work needed to transport ions against a concentration gradient) comes from the internal energy that is released during the reaction. The energy available to do work is the "free energy" (i.e., the ΔG of reaction).

Standard reduction potential

Electrons are transferred in a redox reaction. The transfer occurs from the oxidant to the reductant. As a consequence an electron potential exists between the redox pair.

Recall the change in free energy of a reaction at equilibrium is related to temperature and R (the gas constant).

$$\Delta G^{\circ}_r = -RT \ln K_{eq}$$

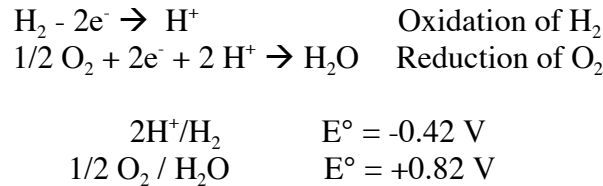
By definition, the electron potential is related to the free energy of reaction.

$$\Delta G^{\circ}_r = nF\Delta E^{\circ} = -RT \ln K_{eq}$$

where n = number of electrons, F = Faraday constant (96.484 kJ/volt g equivalents), and ΔE° is the difference in standard reduction potential between the oxidant and reductant.

E° , the reduction potential is also sometimes called the standard electrode potential. Many standard electron potentials are tabulated in the literature.

Using the examples from above,



In essence this is telling us that O_2 has a high tendency to accept electrons (high reduction potential) and H^+ has a tendency to donate electrons (low reduction potential).

In this case the electrons flow from the H_2 to O_2 .

The overall reaction $1/2 \text{O}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O}$ has a total potential of 1.24 V, which equals 237.34 kJ/mol.

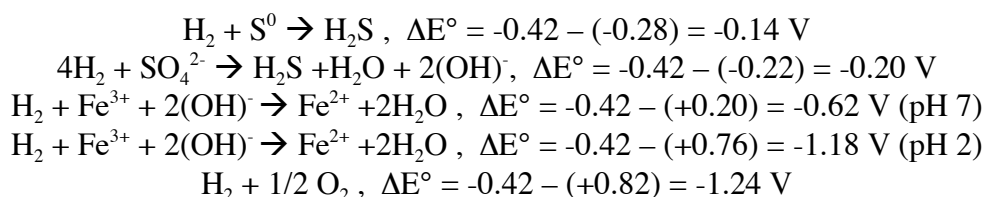
The possible combinations of redox pairs give rise to the concept of the **electron tower**.

The reduced substance in the couple with the lower reduction potential will donate electrons to the oxidized substance with the higher reduction potential (i.e., electrons fall down the tower) The flow of energy, if it is to be used for biosynthesis, must therefore go from oxidant to reductant.

Redox pair	E° volts
CO_2/CO	-0.540
$2\text{H}^+/\text{H}_2$	-0.420
$\text{H}_2\text{CO}_3^*/\text{C}_{org}$	
$\text{H}_2\text{CO}_3^*/\text{CH}_4$	
$\text{S}^0/\text{H}_2\text{S}$	-0.280
$\text{SO}_4^{2-}/\text{H}_2\text{S}$	-0.220

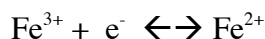
$\text{SO}_3^{2-}/\text{S}^{2-}$	-0.116
$\text{SO}_4^{2-}/\text{FeS}_2$	
$\text{Fe}^{3+}/\text{Fe}^{2+}(\text{pH } 7)$	+0.200
$\text{NO}_2^-/\text{NH}_4^+$	
$\text{NO}_2^-/\text{N}_2\text{O}$	
$\text{NO}_3^-/\text{NO}_2^-$	+0.420
$\text{NO}_3^-/\text{N}_{2(\text{aq})}$	
$\text{Fe}^{3+}/\text{Fe}^{2+}(\text{pH } 2)$	+0.760
$1/2 \text{O}_2 / \text{H}_2\text{O}$	+0.820

Examples with H_2 as the electron donor



Activity of electrons

Let's consider the redox of ferrous and ferric iron and half-cell reaction:



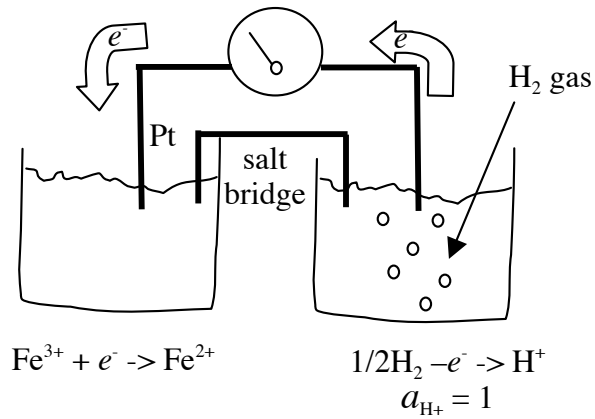
An equilibrium relation can be established where,

$$K_{eq} = \frac{a_{\text{Fe}^{2+}}}{a_{\text{Fe}^{3+}} a_{e^-}}$$

or

$$a_{e^-} = \frac{a_{\text{Fe}^{2+}}}{K_{eq} a_{\text{Fe}^{3+}}}$$

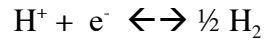
We must define the hydrogen redox potential with the standard hydrogen electrode (SHE), whereby a platinum wire in a H^+ solution at 25°C and 1 atmosphere of hydrogen gas, and by convention the activity of an electron = 1. Other conventions are discussed in Drever's 1997 book on *The geochemistry of natural waters* (3rd edition), Prentice Hall.



We can define the activity of electrons in log form similar to pH, where,

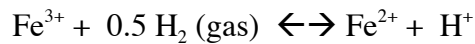
$$pe = -\log_{10} a_{e^-}$$

Now let's consider the redox of hydrogen and half-cell reaction:



$$K_{SHE} = \frac{a_{H_2}^{0.5}}{a_{H^+} a_{e^-}}$$

The overall reaction for iron redox in the electrode system is therefore,



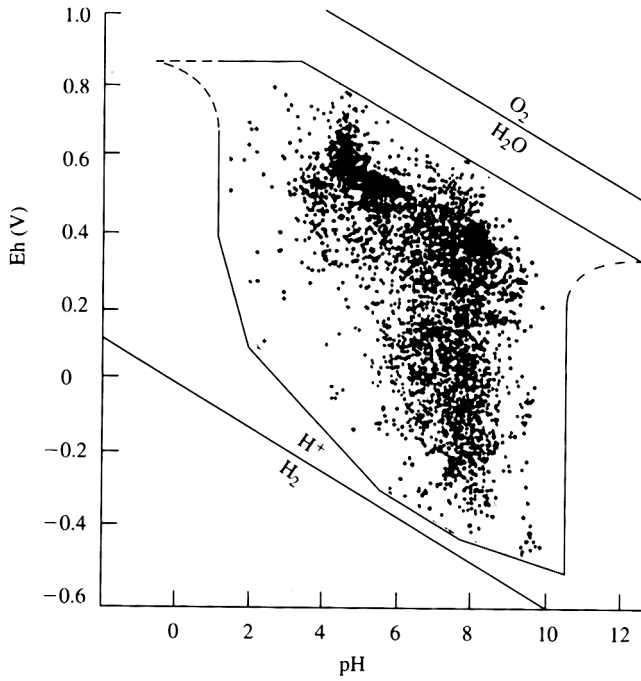
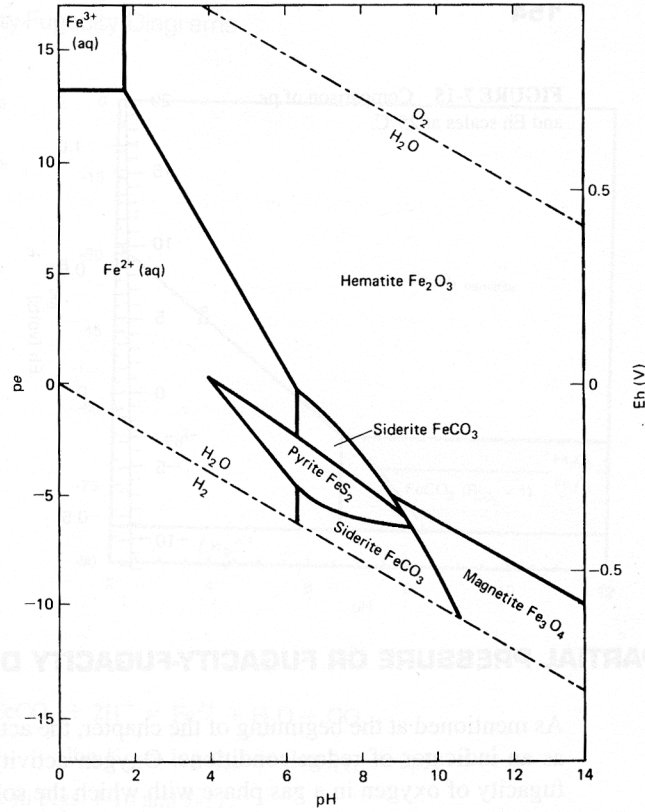
The activity of electrons can be given in units of volts (Eh) or pe.

$$pe = \frac{F}{2.303RT} Eh$$

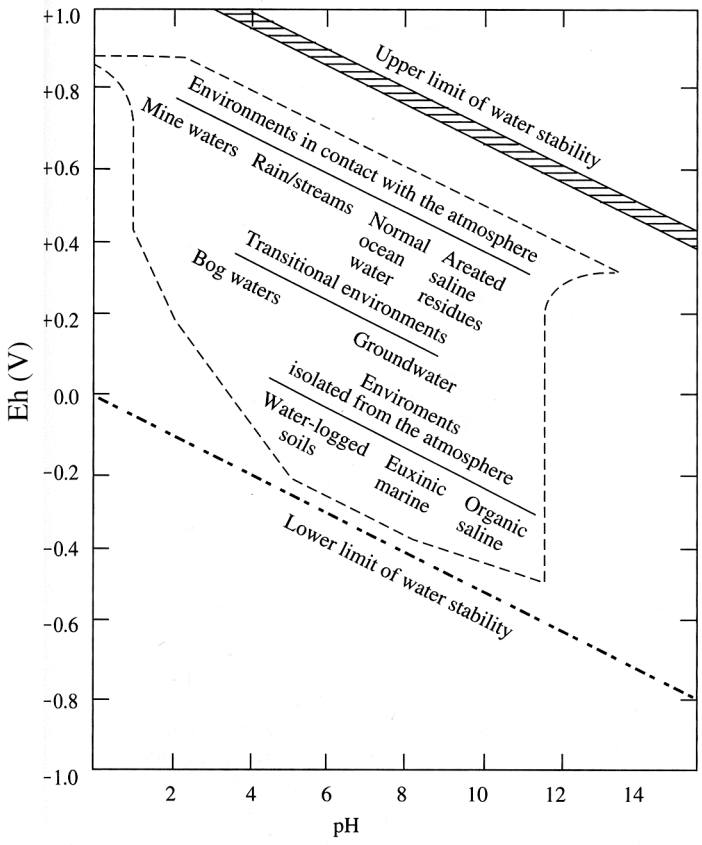
Where F = Faraday's constant (96.484 kJ per volt gram equivalents), R = gas constant (8.314 x 10⁻³ kJ per K.mol).

At 25° C, Eh = 0.059 pe

FIGURE 7-13 Stability relations in the system Fe–O–H₂O–S–CO₂ at 25°C, assuming $\Sigma S = 10^{-6}$, $\Sigma CO_2 = 10^0$ (after Garrels and Christ, 1965). Solid–solution boundaries are drawn for an activity of dissolved Fe species of 10^{-6} .



Locus of measured Eh values. After L. G. M. Baas-Becking et al., Limits of the natural environment in terms of pH and oxidation-reduction potentials, *J. Geol.* 68:243–84. Copyright © 1960 by The University of Chicago Press.



Approximate position of some natural environments in terms of Eh and pH. The dashed line represents the limits of measurements in natural environments, as reported by Baas-Becking et al. (1960) and shown in Fig. 11.3. The crosshatched area defines theoretical conditions under which waters are calculated to contain dissolved oxygen at or above a detection limit of 5 $\mu\text{g/L}$. Modified after R. M. Garrels and C. L. Christ (1965). Solutions, minerals and equilibria. Copyright © 1965 by Freeman, Cooper and Company.