Lecture 11. Redox Chemistry

Many elements in the periodic table can exist in more than one oxidation state. Oxidation states are indicated by Roman numerals in parentheses (e.g. (+I), (-IV) etc.). The oxidation state represents the "electron content" of an element, which can be expressed as the excess or deficiency of electrons relative to the elemental state.

For example:

Element	Oxidation State	Species
Nitrogen	N (+V)	NO_3^-
	N(+III)	NO_2^-
	N(O)	N_2
	N (-III)	NH_3, NH_4^+
Sulfur	S (+VI)	SO_4^{2-}
	S (+II)	$S_2O_3^{2-}$
	S (O)	S^o
	S(-II)	H_2S, HS^-, S^{2-}
Iron	Fe (+III)	Fe^{3+}
	Fe (+II)	Fe^{2+}
Manganese	Mn (+VI)	MnO_4^{2-}
	Mn (+IV)	MnO_2 (s)
	Mn (+III)	MnOOH (s)
	Mn (+II)	Mn^{2+}

Why study **redox** (reduction/oxidation) reactions:
  1. Redox reactions fuel and constrain almost all life processes.
  2. Redox reactions are a major determinant of chemical species present in natural environments.

Redox reactions are characterized by the transfer of electrons between chemical species:
For example, see the following full reaction of cupric ion with metallic zinc (Zn°):
$$Cu^{2+} + Zn^o \Leftrightarrow Cu^o + Zn^{2+}$$
The above **full reaction** can be thought of consisting of two simultaneous **half-reaction**s:
$$Zn^o - 2e^- \Rightarrow Zn^{2+} \quad \text{(an **oxidation** half reaction, electrons lost)}$$
$$Cu^{2+} + 2e^- \Rightarrow Cu^o \quad \text{(a **reduction** half-reaction, electrons gained)}$$
The two species comprising half-reactions (e.g. Zn° & Zn^{2+}) are referred to as a "**couple**".

Redox half-reactions
Redox reactions are written as half-reactions which are in the form of reductions (which means an element is transformed from a higher oxidation state (e.g. +II) to a lower oxidation state (e.g. +I)): $Ox + ne^- = Red$;
Where the more oxidized form of an element is on the left and the reduced form is on the right. n is the number of electrons transferred. We can write an equilibrium constant for

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this reaction as we can for any other reaction. Formally the concentrations should be expressed as activities. Thus: $K = (Red) / (Ox)(e^-)^n$

We can also rearrange the equation to determine the activity of the electron for any redox couple: $(e^-) = [(Red) / K (Ox)]^{1/n}$

Electron activities are usually expressed on either the pE or Eh scales as shown below.

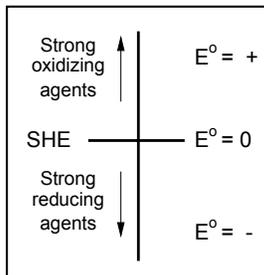$$pE = -\log (e^-) = 1/n \, [\log K - \log (Red)/(Ox)]$$

or

$$Eh = 2.3 \, RT \, pE / F$$

The pE provides a non-dimensional scale (like pH) that expresses the activity of electrons in factors of 10. Eh, called the redox potential, is measured in volts. F is the Faraday constant, which is the electric charge of one mole of electrons (96,500 coulombs). F has a value of 0.059 V at 25°C. With these equations, you can express the energy available from a reaction either in terms of ΔG, Eh or pE.

Standard electrode potentials (E_h°) are convenient reference points for measuring and comparing the relative affinities of chemical substances for electrons under specified conditions. The conventions for E_h°:

  a. E_h° values (units of volts) are compared on the basis of half-reactions, which by convention are <u>written</u> <u>as</u> <u>reductions</u>.
  b. All substances are assumed to be at <u>unit activity</u>.
  c. All E_h° values are determined relative to the reduction potential of the **standard hydrogen electrode** (**SHE**).

SHE

$2 H_+ + 2 e_- = H_2$

$E_o = 0$

$H_2 = (1 \text{ atm})$

Pt electrode

$(H_+) = 1$

Strong oxidizing agents $E^\circ = +$

SHE ——————— $E^\circ = 0$

Strong reducing agents $E^\circ = -$

1. If the E_h° for a given half-reaction is >0, that couple has the potential (under standard conditions) to oxidize the SHE.
2. A negative E_h° indicates a couple that can reduce the SHE (at standard conditions).
3. Tables of E_h° values are found in Libes (p. 112) or Stumm and Morgan (1996, p. 445).
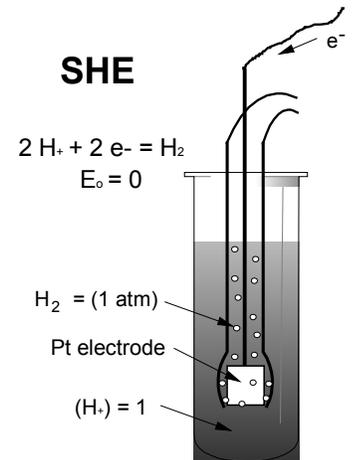
Standard Hydrogen

Thermodynamics:

The basic relationship between E_h° and free energy is:

$$\Delta G_r^\circ = -nFE_h^\circ \qquad \textbf{(1)}:$$

where: ΔG_r° is in **joules (not KJ)**, F = **Faraday's constant** = 96,500 coulombs/mole = the charge of one mole of electrons; and n = the number of moles of e^- transferred. Linking **(1)** into the general free energy equation:

$$\Delta G_r = \Delta G_r^\circ + RT \ln \frac{\pi(\text{products})^a}{\pi(\text{reacants})^b} \qquad \textbf{(2)}$$

$$-\frac{\Delta G_r}{nF} = -\frac{\Delta G_r^{\,o}}{nF} - \frac{RT}{nF} \ln \frac{\pi(\text{products})^a}{\pi(\text{reacants})^b} \qquad \textbf{(3)}$$

$$E_h = E_h{}^o - \frac{RT}{nF} \ln \frac{\pi(\text{products})^a}{\pi(\text{reacants})^b} \qquad \textbf{(4)}$$

at 25 °C and on a $\log_{10}$ basis, with R = 8.314 J/mole degree:

$$E_h = E_h{}^o - \frac{0.0592}{n} \log_{10} \frac{\pi(\text{reduced species})^a}{\pi(\text{oxidized species})^b} \qquad \textbf{(5)}$$

at equilibrium, however, $E_h = 0$, and hence from **(5)** it follows that:

$$E_h{}^o = \frac{0.0592}{n} \log_{10} K \qquad \textbf{(6)}$$

Steps for relating half-reaction voltages and activities from the **Nernst Equation** (**4** or **5**):

a. Write a balanced half-reaction (see below rules in assigning **oxidation numbers**).
b. Determine $\Delta G_r{}^\circ$ (from tabulated $\Delta G_f{}^\circ$ values, using molar coefficients and $\Delta G_f{}^\circ$ of $e^- = 0$)
c. Determine $E_h{}^o$ from $\Delta G_r{}^\circ$, or a given value of K.
d. Use (**4** or **5**) to determine half-reaction E_h, or activities of redox species at equilibrium.

Note from **(1)** that a negative $\Delta G_r{}^\circ$ corresponds to a positive $E_h{}^o$, and thus to a potentially spontaneous reduction half-reaction (at standard conditions) versus the SHE. A positive $\Delta G_r{}^\circ$ indicates a non-spontaneous (impossible) reaction under these conditions.

It is sometimes useful (e.g. for graphics) to define the negative log of electron activity (pE):

$$pE = -\log(e^-) = \frac{FE_h}{2.3RT} = \frac{E_h}{0.0592} = 16.9\ E_h \qquad \textbf{(7)}$$

it follows from combining **(7)** and **(4)** that:

$$\frac{FE_h}{2.3RT} = \frac{FE^o{}_h}{2.3RT} - 1/n \log_{10} \frac{\pi(\text{reduced species})^a}{\pi(\text{oxidized species})^b} \qquad \textbf{(8)}$$

thus:

$$pE = pE^o + 1/n \log_{10} \frac{\pi(\text{oxidized species})^a}{\pi(\text{reduceded species})^b} \qquad \textbf{(9)}$$

Equation **(9)** is useful because it yields straight lines on log activity plots with slopes of 1/n.

We can express the equilibrium constants for half reactions in different forms as well
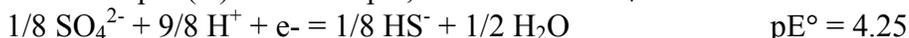$$pE = F\ Eh^o/ 2.3\ RT = 1/n \log K = -1/n\ \Delta G^\circ/ 2.3RT$$

It is most convenient to write the various half reactions in terms of one electron, although this introduces odd fractions for the species coefficients. The species that loses an electron is the e- donor (thus it is oxidized but is a reductant for other elements) and the

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species that accepts an electron is the e- acceptor (so it is reduced but is an oxidant for other species). Some redox half-reactions that may occur in natural waters (with values for pE°= log K) are given in the table on the next page (a more comprehensive table can be found in Morel and Hering, 1993). Note that all half-reactions are written in terms of one electron.

The pE equation can be expressed as: $\quad\quad pE = pE° - \log (Red) / (Ox)$
where pE° can be calculated from log K.

If you know the equilibrium distribution of (Red)/(Ox), this equation can be used to solve for the pE of the environment. Conversely, if you know the pE of the environment, you can calculate the equilibrium activity ratio of the reduced and oxidized forms.

Because the half reactions have different pH dependencies, a common approach is to compare the various half reactions by calculating the equilibrium constant at pH = 7. This constant is called pE°(w). For example, consider the SO_4/HS half reaction:
$$1/8\ SO_4^{2-} + 9/8\ H^+ + e- = 1/8\ HS^- + 1/2\ H_2O \quad\quad\quad pE° = 4.25$$
we can write:
$$pE = pE° - \log (HS^-)^{1/8} / (SO_4^{2-})^{1/8} (H^+)^{9/8} = 4.25 - 1/8 \log (HS^-)/(SO_4^{2-}) + 9/8 \log(H^+)$$
at pH = 7 we calculate pE(w)
$$pE°(w) = pE° + 9/8 \log (H^+)$$
$$pE°(w) = 4.25 - 9/8\ (7) = -3.63$$

RULES FOR ASSIGNING OXIDATION NUMBERS:

1. The sum of all oxidation numbers in an electrically neutral chemical substance must be zero (in H_2S for example, each H atom has an oxidation state of +I, thus the S has an oxidation state of –II).

2. In polyatomic ions, the sum of the oxidation numbers must equal the charge of the ion (for example in NH_4^+, each H atom has an oxidation number of +I thus N has to be –III for the sum to be +1 which is the charge of the ion.

3. The oxidation number of an atom in a monoatomic ion is its charge (Na^+ = +I).

4. The oxidation number of an atom in a single-element neutral substance is 0 (in N_2, O_2 or O_3 the oxidation number is 0).

5. Some elements have the same number in all or nearly all of their compounds. F in a compound is always –I; Compounds of Cl, Br, and I have an oxidation number of –I unless they are combined with oxygen or a halogen of lower atomic number. Oxygen usually has an oxidation number of –II except when it combines with F or with itself. Hydrogen always has an oxidation number of +I when combined with non metals and –I when combined with metals. A metal in group IA of the periodic table always has an oxidation number of +I and a metal in group IIA a number of +II.

6. Metals usually have positive oxidation numbers.

7. A bond between identical atoms in a molecule makes no contribution to the oxidation number of that atom (the electron pair of the bond divide equally.).

TABLE 7.3
Log K, pe^0_w, and $E^0_h(w)$ of Redox Processes[a]

Reaction	$pe^0\ (\equiv log\ K)$	pe^{0a}_w	$E^0_h(w)$
(1) $\frac{1}{4}O_2(g) + H^+ + e^- = \frac{1}{2}H_2O$	+20.75	+13.75	+0.81
(2) $\frac{1}{5}NO_3^- + \frac{6}{5}H^+ + e^- = \frac{1}{10}N_2(g) + \frac{3}{5}H_2O$	+21.05	+12.65	+0.75
(3) $\frac{1}{2}MnO_2(s) + \frac{1}{2}HCO_3^-(10^{-3}M) + \frac{3}{2}H^+ + e^- = \frac{1}{2}MnCO_3(s) + \frac{3}{8}H_2O$	—	+3.9[b]	+0.23
(4) $\frac{1}{2}NO_3^- + H^+ + e^- = \frac{1}{2}NO_2^- + \frac{1}{2}H_2O$	+14.15	+7.15	+0.42
(5) $\frac{1}{8}NO_3^- + \frac{5}{4}H^+ + e^- = \frac{1}{8}NH_4^+ + \frac{3}{8}H_2O$	+14.90	+6.15	+0.36
(6) $\frac{1}{6}NO_2^- + \frac{4}{3}H^+ + e^- = \frac{1}{6}NH_4^+ + \frac{1}{3}H_2O$	+15.14	+5.82	+0.34
(7) $\frac{1}{2}CH_3OH + H^+ + e^- = \frac{1}{2}CH_4(g) + \frac{1}{2}H_2O$	+9.88	+2.88	+0.17
(8) $\frac{1}{4}CH_2O + H^+ + e^- = \frac{1}{4}CH_4(g) + \frac{1}{4}H_2O$	+6.94	−0.06	+0.00
(9) $FeOOH(s) + HCO_3^-(10^{-3}M) + 2H^+ + e^- = FeCO_3(s) + 2H_2O$	—	−0.8[b]	−0.05
(10) $\frac{1}{2}CH_2O + H^+ + e^- = \frac{1}{2}CH_3OH$	+3.99	− 3.01	−0.18
(11) $\frac{1}{6}SO_4^{2-} + \frac{4}{3}H^+ + e^- = \frac{1}{6}S(s) + \frac{2}{3}H_2O$	+6.03	−3.30	−0.20
(12) $\frac{1}{8}SO_4^{2-} + \frac{5}{4}H^+ + e^- = \frac{1}{8}H_2S(g) + \frac{1}{2}H_2O$	+5.25	−3.50	−0.21
(13) $\frac{1}{8}SO_4^{2-} + \frac{9}{8}H^+ + e^- = \frac{1}{8}HS^- + \frac{1}{2}H_2O$	+4.25	−3.75	−0.22
(14) $\frac{1}{2}S(s) + H^+ + e^- = \frac{1}{2}H_2S(g)$	+2.89	−4.11	−0.24
(15) $\frac{1}{8}CO_2(g) + H^+ + e^- = \frac{1}{8}CH_4(g) + \frac{1}{4}H_2O$	+2.87	−4.13	−0.24
(16) $\frac{1}{6}N_2(g) + \frac{4}{3}H^+ + e^- = \frac{1}{3}NH_4^+$	+4.68	−4.68	−0.28
(17) $\frac{1}{2}(NADP^+) + \frac{1}{2}H^+ + e^- = \frac{1}{2}(NADPH)$	−2.0	−5.5	−0.33
(18) $H^+ + e^- = \frac{1}{2}H_2(g)$	0.0	−7.00	−0.41
(19) Oxidized ferredoxin + e^- = reduced ferredoxin	−7.1	−7.1	−0.42
(20) $\frac{1}{4}CO_2(g) + H^+ + e^- = \frac{1}{24}(glucose) + \frac{1}{4}H_2O$	−0.20	−7.20	−0.43
(21) $\frac{1}{2}HCOO^- + \frac{3}{2}H^+ + e^- = \frac{1}{2}CH_2O + \frac{1}{2}H_2O$	+2.82	−7.68	−0.45
(22) $\frac{1}{4}CO_2(g) + H^+ + e^- = \frac{1}{4}CH_2O + \frac{1}{4}H_2O$	−1.20	−8.20	−0.48
(23) $\frac{1}{2}CO_2(g) + \frac{1}{2}H^+ + e^- = \frac{1}{2}HCOO^-$	−4.83	−8.33	−0.49

Source: From *Aquatic Chemistry*, W. Stumm and J. J. Morgan, copyright © 1970 by John Wiley & Sons, Inc., New York, p. 318. Reprinted by permission. See Stumm and Morgan (1970) for data sources.
[a]Values for pe^0_w apply to the electron activity for unit activities of oxidant and reductant in neutral water, that is, at pH = 7.0 for 25°C.
[b]These data correspond to $(HCO_3^-) = 10^{-3}\ M$ rather than unity and so are not exactly pe^0_w; they represent typical aquatic conditions more nearly than pe^0_w values do.

Full reactions:
Half-reactions don't occur alone in the real world because free electrons don't exist for long in any number. Thus, half-reactions are actually coupled together into full reactions characterized by a **total potential difference**, ΔE, which is equal in magnitude to the sum of the half-cell potentials (E_h), <u>after</u> the sign of the oxidation half-reaction has been <u>reversed</u>:

$$\Delta E = (E_{h\text{-red}} - E_{h\text{-ox}}) = (E^o{}_{h\text{-red}} - E^o{}_{h\text{-ox}}) - \frac{0.0592}{n} \log_{10} \frac{\pi(\text{products})^a}{\pi(\text{reactants})^b}$$

Thus, for the reaction on the top of page 1:

$$\Delta E = (E^o{}_{hCu2+\rightarrow Cu^\circ} - E^o{}_{hZn2+\rightarrow Zn^\circ}) - \frac{0.0592}{2} \log_{10} \frac{(Zn^{2+})}{(Cu^{2+})}$$

Redox Calculations
There are two main types of redox calculations. The first is the calculation of what controls the pE of the environment. This is analogous to calculating the pH of the environment, for example when it is controlled by the H_2CO_3 system in equilibrium with atmospheric P_{CO2}. The second type of calculation is to determine how trace species respond or distribute themselves with respect to that pE. Again by analogy, when we know the pH, we can calculate the pH dependent speciation of trace species, like Fe for example.

What sets the pE in the ocean at pH ~ 8 and pO$_2$ 0.2 atm?
Probably the O_2 / H_2O couple, this is the typical pE for oxic conditions.

$O_2 + 4H^+ + 4e^- \Longleftrightarrow 2\,H_2O$ $E° = 1.229$
                                                $\log K = 83.1$
                                                $n=4$

$$K = \frac{(H_2O)^2}{(e^-)^4(H^+)^4\,pO_2}$$

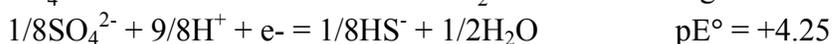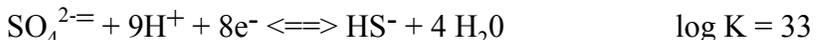$\log K = 2 \log (H_2O) - \log pO_2 - 4 \log (H^+) - 4 \log (e^-)$

$83 = \quad 0 \quad\quad\quad\quad\quad -(-0.68) +4pH \quad\quad + 4pE$

where $(H_2O) \approx 1$ (=1.0 in distilled water; 0.98 in seawater)
      $pO_2 = 0.21$ atm $pH \approx 8.0$ to 8.2
So, $pE = (83 - 0.68 - 32)/4 = 12.4$ to 12.6, depending on pH. Positive pE in an oxidizing environment.

What is the pE of water at pH = 8 in equilibrium with the SO_4/H_2S couple (e.g. anoxic waters)? Assume that $HS^- = 10^{-5}$ and $SO_4^{2-} = 10^{-3}$. This is typical for the anoxic end-member condition.
$SO_4^{2-} + 9H^+ + 8e^- \Longleftrightarrow HS^- + 4\,H_2O$ $\log K = 33$
$1/8 SO_4^{2-} + 9/8 H^+ + e^- = 1/8 HS^- + 1/2 H_2O$ $pE° = +4.25$
$pE = pE° - \log (HS\text{-})^{1/8} / (SO_4^{2-})^{1/8} (H^+)^{9/8}$
$pE = pE° - 1/8 \log (HS^-) + 1/8 \log (SO_4^{2-}) + 9/8 \log (H^+)$
$pE = 4.25 + 0.63 - 0.37 - 9/8 pH$
$pE = 4.25 + 0.63 - 0.37 - 9.0$
$pE = -4.49$
The more negative the pE the more "reducing" the environment.
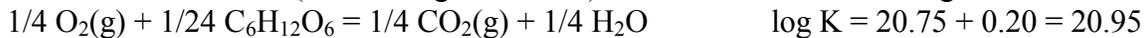
Balanced Redox Reactions

The equilibrium constant for an oxidation-reduction reaction can be determined by combining the constants from the ½ cell reaction table as follows.

Say we want to study the reaction of oxygen with glucose. The two half reactions (written as reductions in terms of one electron) with their appropriate values of log K, are:

(Rxn1) $1/4\ O_2(g) + H^+ + e- = H_2O$ $\qquad\qquad\qquad\qquad$ $pE° = \log K = 20.75$

(Rxn2) $1/4\ CO_2(g) + H^+ + e- = 1/24\ C_6H_{12}O_6 + 1/4\ H_2O$ $\qquad$ $pE°= -0.20$

We reverse reaction 2 (now it's log K = +0.20) and add it to reaction 1 to get:

$1/4\ O_2(g) + 1/24\ C_6H_{12}O_6 = 1/4\ CO_2(g) + 1/4\ H_2O$ $\qquad$ $\log K = 20.75 + 0.20 = 20.95$

or

$6O_2(g) + C_6H_{12}O_6 = 6CO_2(g) + 6H_2O$ $\qquad\qquad\qquad$ $\log K = 20.95 \times 24 = 502.80$

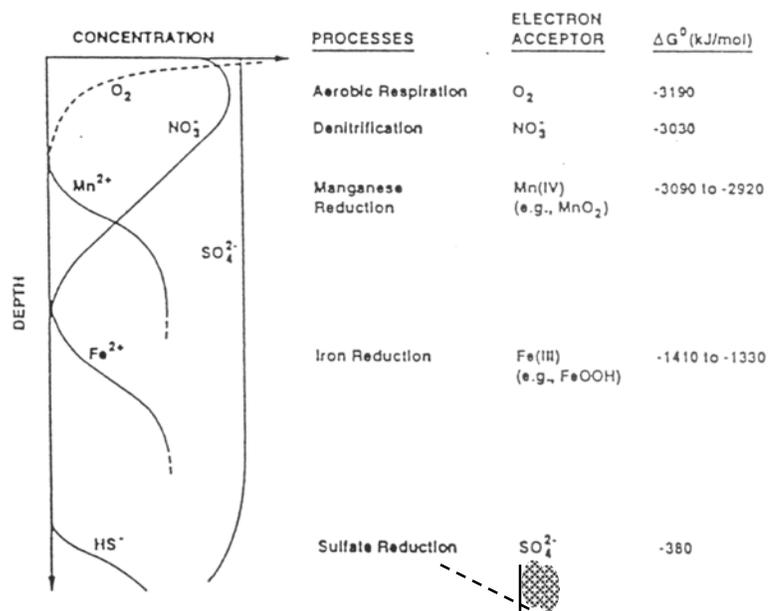Several important natural oceanic processes can be described in terms of redox reaction.

Photosynthesis and Oxidation:

Photosynthesis makes simultaneously one of the most reducing materials in nature (organic matter) and one of the most oxidizing (O_2). There are, however, many potential oxidizing agents in addition to O_2 (e.g. MnO_2, NO_3^-, FeOOH, SO_4^{2-}, CO_2), which are typically utilized by microorganisms in the sequence of their greatest free energy potential. Organisms are restricted in the oxidizing agents and reducing substrates they use. Animals use O_2, whereas microorganisms are also capable of using use a variety of the lower-yield electron acceptors.

There is an "ideal" sequence of redox reactions based on the energy available. In this sequence, organic matter is combusted in order by O_2, NO_3, MnO_2, Fe_2O_3 then SO_4^{2-} to provide this energy. Most of these reactions have slow kinetics if left to occur on their own. Bacteria mediate most of these reactions and get the energy for their life processes. Because the energy of the sun is trapped in the C-C bonds (by photosynthesis), bacteria are indirectly using sunlight when they "combust" or oxidize natural organic matter to CO_2. Using the half-reactions we can calculate the log K and log K_w values for generic organic matter (CH_2O) oxidation by various oxidants (or electron acceptors).

Oxidation-Reduction reaction	log K	log K_w
Aerobic Respiration		
$1/4CH_2O + 1/4O_2 = 1/4H_2O + 1/4CO_2(g)$	20.95	20.95
Denitrification		
$1/4CH_2O + 1/5NO_3^- + 1/5H^+ = 1/4CO_2(g) + 1/10N_2(g) + 7/20H_2O$	21.25	19.85
Manganese Reduction		
$1/4CH_2O + 1/2MnO_2(s) + H^+ = 1/4CO_2(g) + 1/2Mn^{2+} + 3/4H2O$	21.0	17.0
Iron Reduction		
$1/4CH_2O + Fe(OH)_3(s) + 2H^+ = 1/4CO_2(g) + Fe^{2+} + 11/4H_2O$	16.20	8.2
Sulfate Reduction		
$1/4CH_2O + 1/8SO_4^{2-} + 1/8H^+ = 1/4CO_2(g) + 1/8HS^- + 1/4H_2O$	5.33	3.7
Methane Fermentation		
$1/4CH_2O = 1/8CO_2(g) + 1/8CH_4$	3.06	3.1

These reactions proceed with burial depth in marine sediments and are considered the "diagenetic redox sequence". These reactions result in oxidation of organic matter in marine sediments.

CONCENTRATION	PROCESSES	ELECTRON ACCEPTOR	ΔG^0 (kJ/mol)
O_2	Aerobic Respiration	O_2	-3190
NO_3^-	Denitrification	NO_3^-	-3030
Mn^{2+}	Manganese Reduction	$Mn(IV)$ (e.g., MnO_2)	-3090 to -2920
SO_4^{2-}			
Fe^{2+}	Iron Reduction	$Fe(III)$ (e.g., $FeOOH$)	-1410 to -1330
HS^-	Sulfate Reduction	SO_4^{2-}	-380

DEPTH

An example for the water column of Saanich Inlet where the surface water is oxic and the bottom water column is anoxic. The figure shows the depth profiles in the water column of : O_2, H_2S, Nitrogen species, Iodine species, Fe^{2+} and Mn^{2+}.

Data from Emerson et al. (1979) Deep-Sea Res 26A, 859-878.
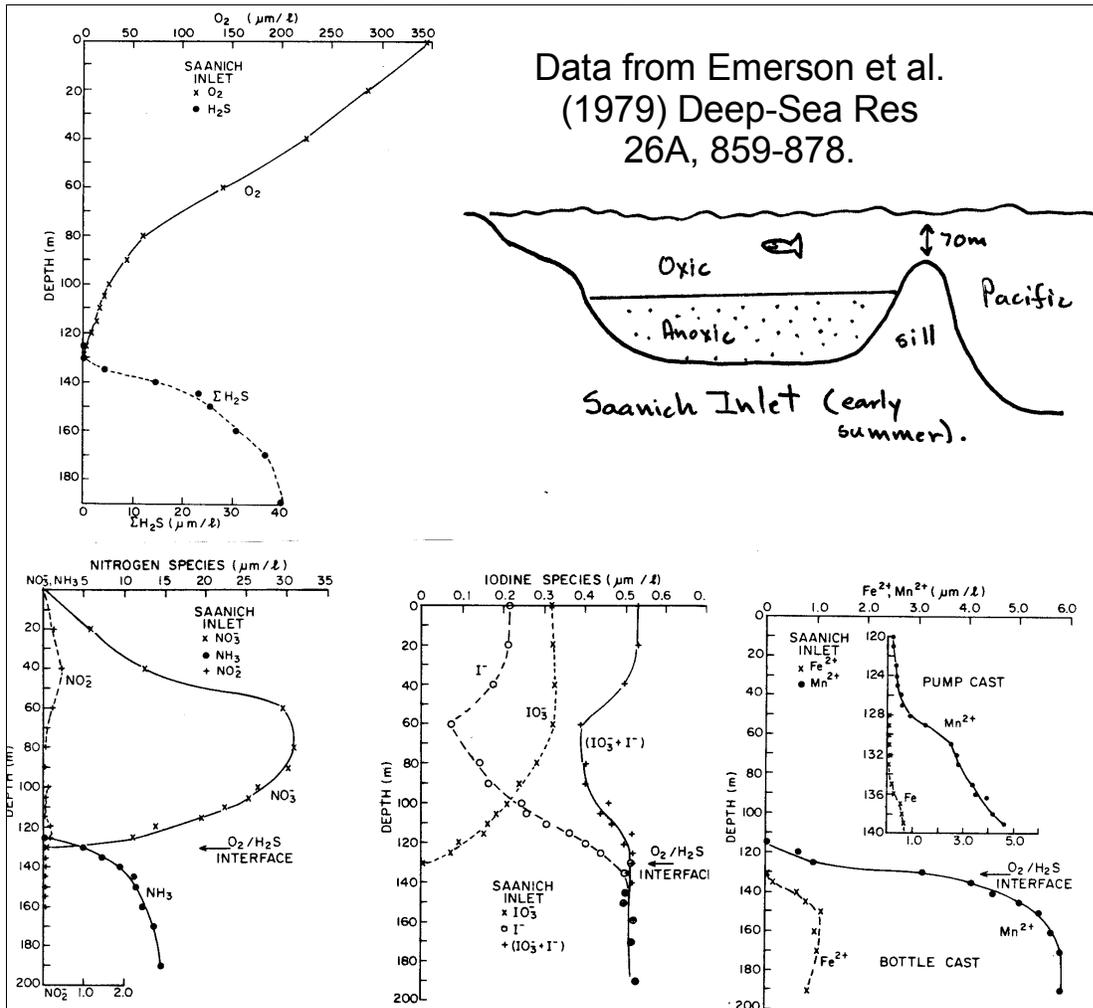
Diagenesis: Chemical and physical changes or reactions that occur in sediments following deposition and burial.

Physical changes include:

> **Compaction** – porosity or the amount of open space (water) in between the grains of sediment decreases with depth.
>
> **Winnowing** – bottom currents redistribute the sediments.
>
> **Bioturbation** – mixing by biological organisms. Depth of bioturbation depends on environment. Typically 5-10 cm for pelagic (open ocean) sediments; 30-50 cm or more for coastal environments.

The most important diagenetic reactions are chemical transformations after burial. Some diagenetic reactions are driven by redox reactions; in particular, the oxidation of organic matter is a primary reaction occurring in surficial sediments, as discussed previously. Diagenetic alteration continues with depth: the soft sediments lithify and re-crystallize. $CaCO_3$ ooze become chalk or limestone and the opal turns into chert. The water that is trapped between the grains (pore water) reacts with the minerals and the original chemistry and mineralogy of the sediment can be changes. Carbonates loose some Sr and Ca and pick up Mg. Organic matter forms petroleum.