Readings:
Schlesinger Chapter 7; Erwin (2009)

I. Redox Biogeochemistry in Aquatic Systems

II. Wetlands & Layered Microbial Habitats

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**Aquatic redox**

Oxidation-Reduction Chemistry Review
- Oxidation states, balancing equations
- Oxic-anoxic & redox potential
- Simple electrochemical cell

Redox reactions
- Chemical speciation
- Eh – pH diagrams
- Redox reactions in nature

Biogeochemical reactions and their thermodynamic control
- Redox sequence of OM oxidation in aquatic environments
- Leading into wetlands, vertical profiles, time-series, and layered microbial habitats…

**Wetlands & layers**

Emphasize organic matter cycling
- e- donor, Storage
- Microbial metabolic pathways

Wetland habitats (& other layered microbial habitats)
- Types of wetlands
- Hydrology, soils,
- vegetation, productivity

Global change threats to wetlands
- Development
- Saltwater intrusion
- Temperature & CO₂
Definitions for today

Oxidation –
Reduction –
Reductant –
Oxidant –
Oxidation state (number) –
Oxidation-reduction potential –
Gibbs Free Energy –
Many elements in the periodic table can exist in more than one oxidation state. **Oxidation states** are indicated by Roman numerals (e.g. (+I), (-II), 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.

If we want to determine whether a reaction is oxidation or reduction, we need to know the oxidation number of the element & how it changes

*n.b.*, ‘valence’, ‘oxidation number’ and ‘formal charge’ are commonly used interchangeably, but are actually distinct from one another. For our purposes, we are only dealing with oxidation number
Rules for determining oxidation number of an element

(1) Oxidation state of an element in its elementary state = 0
e.g., Cl₂, Na, P…etc.

(2) Oxidation state of an element in a monatomic (one one atom) ion is equal to the charge on the ion
e.g., Na⁺ = +1; Cl⁻ = -1; Fe³⁺ = +3

(3) Oxidation state of certain elements is the same in all, or almost all of their compounds
e.g., Group 1A elements: Li, Na, K, Rb, Cs =+1
Group 2A elements: Be, Mg, Ca, Sr, Ba, Ra = +2
Group VII b elements: F, Cl, Br, I, At = -1 in binary compounds

Oxygen is almost always -2 (Except: when bonded to O or F)
H is almost always +1; Except with a metal, e.g. NaH, CaH₂ is -1
(4) The sum of the oxidation states in a neutral species is = 0; In a charged ion it is equal to the charge on the ion
e.g., \( \text{Na}_2\text{Se} \): \( \text{Na} = +1 \times 2 = 2 \), thus \( \text{Se} = -2 \)
\( \text{MnO}_4^- \): \( \text{O} = -2 \times 4 = -8 \), thus \( \text{Mn} = 8 - 1 = 7 \)

(5) Fractional oxidation numbers are possible.
e.g., in \( \text{Na}_2\text{S}_4\text{O}_6 \) (sodium tetrathionate), \( S \) has an oxidation number of \( +10/4 \)
\( \text{O}: 6(-2) = -12 \)
\( \text{Na}: 2(+1) = 2 \)
Residual = -10, which must be balanced by \( S: 4(+10/4) = +10 \)

(6) The oxidation number is designated by:
   Arabic number below the atom, or
   Roman numeral or Arabic number after the atom (in parentheses)
Many elements in the periodic table can exist in more than one oxidation state. **Oxidation states** are indicated by Roman numerals (e.g. (+I), (-II), 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.

### Oxidation States

<table>
<thead>
<tr>
<th>Element</th>
<th>Oxidation State</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td></td>
<td>NO$_3^-$, NO$_2^-$, N$_2$, NH$_3$, NH$_4^+$</td>
</tr>
<tr>
<td>Sulfur</td>
<td></td>
<td>SO$_4^{2-}$, S$_2$O$_3^{2-}$, S$^\circ$, H$_2$S, HS$^-$, S$^{2-}$</td>
</tr>
<tr>
<td>Iron</td>
<td></td>
<td>Fe$^{3+}$, Fe$^{2+}$</td>
</tr>
<tr>
<td>Manganese</td>
<td></td>
<td>MnO$_4^{2-}$, MnO$_2$ (s), MnOOH (s), Mn$^{2+}$</td>
</tr>
</tbody>
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<tr>
<td>Nitrogen</td>
<td>N (+V)</td>
<td>NO₃⁻</td>
</tr>
<tr>
<td></td>
<td>N (+III)</td>
<td>NO₂⁻</td>
</tr>
<tr>
<td></td>
<td>N (O)</td>
<td>N₂</td>
</tr>
<tr>
<td></td>
<td>N (-III)</td>
<td>NH₃, NH₄⁺</td>
</tr>
<tr>
<td>Sulfur</td>
<td>S (+VI)</td>
<td>SO₄²⁻</td>
</tr>
<tr>
<td></td>
<td>S (+II)</td>
<td>S₂O₃²⁻</td>
</tr>
<tr>
<td></td>
<td>S (O)</td>
<td>S°</td>
</tr>
<tr>
<td></td>
<td>S(-II)</td>
<td>H₂S, HS⁻, S²⁻</td>
</tr>
<tr>
<td>Iron</td>
<td>Fe (+III)</td>
<td>Fe³⁺</td>
</tr>
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<tr>
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<td>Mn (+IV)</td>
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<td>Mn²⁺</td>
</tr>
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</table>

Assign O to be (-II) & H to be (+I), calculate.
Balancing oxidation-reduction reactions

Conventionally always put the oxidised species on the left, the reduced species on the right.

e.g. $\text{MnO}_4^- \text{ (aq)} + \text{Cl}^- \text{ (aq)} = \text{Mn}^{2+} \text{ (aq)} + \text{Cl}_2 \text{(g)}$

1. Separate the reaction into a reduction and oxidation part

   $\text{MnO}_4^- \text{ (aq)} = \text{Mn}^{2+} \text{ (aq)}$ redox
   $\text{Cl}^- \text{ (aq)} = + \text{Cl}_2 \text{(g)}$ oxidation

2. Balance each 1/2 reaction with respect to mass then with respect to charge. Use $e^-$, $H^+$, $H_2O$ or $OH^-$

   $2\text{Cl}^- \text{ (aq)} = \text{Cl}_2 \text{ (g)}$ mass
   $2\text{Cl}^- \text{ (aq)} = \text{Cl}_2 \text{ (g)} + 2e^-$ mass + charge
Balancing oxidation-reduction reactions

\[ \text{MnO}_4^{-}(aq) = \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O} \ \text{(mass oxygen)} \]

\[ \text{MnO}_4^{-}(aq) + 8\text{H}^{+} = \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O} \ \text{(mass oxygen + hydrogen)} \]

\[ \text{MnO}_4^{-}(aq) + 8\text{H}^{+} + 5e^{-} = \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O} \ \text{(mass + charge)} \]

3. Combine half reactions so electron gain equals loss

\[ 5\times A = 10 \ e^{-}; \ 2\times B = 10 \ e^{-} \ i.e. \ 5\times A + 2\times B \]

\[ 10 \ \text{Cl}^{-}(aq) + 2\text{MnO}_4^{-} + 16\text{H}^{+} = 5\text{Cl}_2(g) + 2\text{Mn}^{2+}(aq) + 8\text{H}_2\text{O} \]

4. Check for atom and charge balance
Oxic: \([O_2] > 100 \mu M\)

- Oxidation of OM by molecular oxygen
- Relatively low OM (especially continental fluvial sediments) because the OM is partially oxidized prior to sediment burial
- Fe-oxy-hydroxide phases are not reduced -- they are transformed to hematite \((Fe_2O_3)\) during diagenesis (e.g., Red beds)
- Presence of oxidized Mn phases
- Usually light brown sediment
Suboxic: 100 µM > [O₂] > 1 µM

Non-sulfidic environment -- [H₂S] < 1 µM

- Although the oxidation of OM consumes O₂, there is insufficient OM to generate much H₂S

- NO₃⁻, MnO₂, and FeOX reduction

- Fe²⁺ and Mn²⁺ increase and become supersaturated with respect to *siderite* (FeCO₃), *rhodochrosite* (MnCO₃), *glauconite* ((K,Na)(Fe³⁺,Al,Mg)₂(Si,Al)₄O₁₀(OH)₂), and *vivianite* (Fe₃(PO₄)₂·8(H₂O))

- Usually grey sediment
Anoxic: [O$_2$] < 1 µM

1) Sulfidic environments -- [H$_2$S] > 1 µM

Oxidation of OM is by sulfate reduction

- *Greigite* (Fe$_3$S$_4$) and *mackinawite* (Fe$_{Hx}$S) are first formed metastably, then react with H$_2$S to produce *iron monosulfide* (FeS) and *pyrite* (FeS$_2$).

- *Alabandite* (MnS) is only stable under very high concentrations of H$_2$S -- thus *rhodochrosite* (MnCO$_3$) is more common

- Requires large OM deposition rate

- Usually black sediment
Redox Potential: The Fundamentals

- **Redox potential** expresses the tendency of an environment to receive or supply electrons.

  - An *oxic* environment has high redox potential because $O_2$ is available as an *electron acceptor*.

    For example, Fe oxidizes to rust in the presence of $O_2$ because the iron shares its electrons with the $O_2$:

    $$4Fe + 3O_2 \rightarrow 2Fe_2O_3$$

  - In contrast, an *anoxic* environment has low redox potential because of the absence of $O_2$.

  > *the more positive the potential, the greater the species' affinity for electrons and tendency to be reduced*
A Simple Electrochemical Cell

- FeCl$_2$ at different Fe oxidation states in the two sides
- Wire with inert Pt at ends -- voltmeter between electrodes
- Electrons flow along wire, and Cl$^-$ diffuses through salt bridge to balance charge
- Voltmeter measures electron flow
- Charge remains neutral
- Container on right side is more oxidizing and draws electrons from left side

Electron flow and Cl\(^{-}\) diffusion continue until an equilibrium is established – steady voltage measured on voltmeter

If container on right also contains O\(_2\), Fe\(^{3+}\) will precipitate and greater voltage is measured

\[
4\text{Fe}^{3+} + 3\text{O}_2 + 12\text{e}^- \rightarrow 2\text{Fe}_2\text{O}_3 (s)
\]

- The voltage is characteristic for any set of chemical conditions
Redox Potential in Nature

• A mixture of constituents, not really separate cells

• We insert an inert *Pt electrode* into an environment and measure the voltage relative to a standard electrode

  [Std. electrode = $H_2$ gas above solution of known pH (theoretical, not practical). More practical electrodes are calibrated using this $H_2$ electrode.]

  – Example: when $O_2$ is present, electrons migrate to the Pt electrode:

  \[
  O_2 + 4e^- + 4H^+ \rightarrow 2H_2O
  \]

  – The electrons are generated at the $H_2$ electrode:

  \[
  2H_2 \rightarrow 4H^+ + 4e^-
  \]

• Voltage between electrodes measures the *redox potential*
Redox Potential in Nature

Schlesinger - Fig. 7.13
Redox Potential of a Reaction

• General reaction:

\[
\text{Oxidized species} + e^- + H^+ \leftrightarrow \text{reduced species}
\]

• Redox is expressed in units of “pe,” analogous to pH:

\[
pe = - \log \{e^-\} \quad (\text{or} \quad Eh = 2.3 \, RT \, pE/F)
\]

where \([e^-]\) is the electron concentration or activity

• “pe” is derived from the equilibrium constant \((K)\) for an oxidation-reduction reaction at equilibrium:

\[
K = \frac{[\text{reduced species}]}{[\text{oxidized species}][e^-][H^+]} 
\]
If we assume \([\text{oxidized}] = [\text{reduced}] = 1\) (i.e., at standard state), then:

\[
\log K = \log [\text{red}] - \log [\text{ox}] - \log [e^-] - \log [H^+] = -p_{\text{red}} + p_{\text{ox}} + p_e + pH
\]
$$ \log K = pe + pH $$

The Nernst Equation can be used to relate this equation to measured Pt-electrode voltage ($E_h$, $E_h$, $E_H$):

$$ pe \equiv pE = \frac{F}{2.3RT} Eh \quad \text{or} \quad Eh = 2.3 \, RT \, pE/F $$

where:

- $Eh$ = measured redox potential as voltage
- $R$ = the Universal Gas Constant ($= 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$)
- $T$ = temperature in degrees Kelvin
- $F$ = Faraday Constant ($= 23.1 \text{ kcal V}^{-1} \text{ equiv}^{-1}$)
- $2.3$ = conversion from natural to base-10 logarithms
• Reducing solution
  – Electron activity is high
  – pe is low
  – High tendency to donate electrons

• Oxidizing solution
  – Electron activity is low
  – pe is high
  – High tendency to accept electrons

• All very analogous to treatment of pH
Eh- pH (pe – pH) Diagrams

- Used to show equilibrium speciation for reactants as functions of Eh and pH
- Red lines are practical Eh-pH limits on Earth
- \( pE = pe = \frac{F}{2.3RT} Eh \)
Eh-pH diagrams describe the thermodynamic stability of chemical species under different biogeochemical conditions.

Example – **predicted** stable forms of Fe in aqueous solution:

Diagram is for 25 degrees C
Example –
Oxidation of $\text{H}_2\text{S}$ released from anoxic sediments into oxic surface water:
Redox Reactions in Nature

• Example: net reaction for aerobic oxidation of organic matter:

\[ \text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]

• In this case, oxygen is the **electron acceptor** – the half-reaction is:

\[ \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \]

• Different organisms use different electron acceptors, depending on availability due to local redox potential

• The more oxidizing the environment, the higher the **energy yield** of the OM oxidation (the more negative is ΔG, the Gibbs free energy)
Free Energy and Electropotential

• Talked about electropotential (aka emf, Eh) --> driving force for e⁻ transfer

• How does this relate to driving force for any reaction defined by $\Delta G_r$??

\[ \Delta G_r = - n \mathcal{F} E \]

– Where $n$ is the # of e⁻’s in the rxn, $\mathcal{F}$ is Faraday’s constant (23.06 cal V⁻¹), and $E$ is electropotential (V)

• $pE$ for an electron transfer between a redox couple analogous to $pK$ between conjugate acid-base pair
• The higher the energy yield, the greater the benefit to organisms that harvest the energy

• In general:
  – There is a temporal and spatial sequence of energy harvest during organic matter oxidation
  – Sequence is from the use of high-yield electron acceptors to the use of low-yield electron acceptors
The greater the difference in $\Delta G^\circ$ between the oxidizing & reducing agents, the greater the free energy yield for the reaction.

Sets up a sequence of favorable oxidants for organic matter oxidation.

Organic matter oxidation by $O_2$ is greatest free energy yield.

**Why is organic matter such a good electron donor?**
Z-scheme for photosynthetic electron transport

Energy from sun converted to C-C, energy rich, chemical bonds

Falkowski and Raven (1997)
# Environmentally Important Organic Matter Oxidation Reactions

<table>
<thead>
<tr>
<th>Reducing Half-reaction</th>
<th>$E_n$ (V)</th>
<th>$\Delta G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduction of $O_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$</td>
<td>+0.812</td>
<td>-29.9</td>
</tr>
<tr>
<td>Reduction of $NO_3^-$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2NO_3^- + 6H^+ + 6e^- \rightarrow N_2 + 3H_2O$</td>
<td>+0.747</td>
<td>-28.4</td>
</tr>
<tr>
<td>Reduction of Mn (IV)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$</td>
<td>+0.526</td>
<td>-23.3</td>
</tr>
<tr>
<td>Reduction of Fe (III)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Fe(OH)_3 + 3H^+ + e^- \rightarrow Fe^{2+} + 3H_2O$</td>
<td>-0.047</td>
<td>-10.1</td>
</tr>
<tr>
<td>Reduction of $SO_4^{2-}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$SO_4^{2-} + 10H^+ + 8e^- \rightarrow H_2S + 4H_2O$</td>
<td>-0.221</td>
<td>-5.9</td>
</tr>
<tr>
<td>Reduction of $CO_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$</td>
<td>-0.244</td>
<td>-5.6</td>
</tr>
</tbody>
</table>