Thermodynamics of Biogeochemical Reactions

Microbial Biogeochemistry & Global Change
SWES 410/510

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How define **biogeochemical reactions**?

- Reactions that involve biological *and* geochemical
  - **reactants** (e.g., biomolecules and minerals)
  - **products** (organo-mineral complexes, biominerals)
- Biotic (abiotic) mediation of inorganic (organic) transformations (e.g., production of AMD, oxidation of polyphenols on Mn$^{IV}$ oxide surfaces)
- Include
  - Adsorption-Desorption
  - Dissolution-Precipitation
  - Reduction-Oxidation

TEM image of Fe hydroxide encrusted *Leptothrix ochracea* cells from a seep in Denmark (Emerson, 2000)
Organic matter is primary source of reducing power in aqueous environments.

E.g., Respiration: \( \text{CH}_2\text{O} (s) + \text{O}_2 (g) = \text{CO}_2 (g) + \text{H}_2\text{O} (l) \)
Spatial Variability in Redox Status

Figure 5–4. Characteristics of many wetland soils showing a shallow oxidized soil layer over a reduced soil layer, and soil profiles of sodium acetate-extractable manganese, ferrous iron, sulfide, and redox potential. (After Patrick and Delaune, 1972, and Gambrell and Patrick, 1978)
Geomedia are highly heterogeneous in redox status

- Many of the reactions responsible for this heterogeneity are catalyzed by microbes.
- Consumption of $O_2$ (g)
- Alternative terminal electron accepting processes (TEAPs)
- Changes pH
- Changes in Eh (or pe)
- Changes in element speciation
- Affects speciation and solubility of
  - Major elements: C, N, O, S, Mn, Fe
  - Contaminant/trace elements: As, Se, Cr, Hg, U, Cu, Mo, Au, Ag and Pb.
Chemical Thermodynamics

• The primary objective of chemical thermodynamics is the establishment of a criterion for the determination of the feasibility or spontaneity of a given transformation.
  - Chemical reactions
  - Phase changes
  - Formation of solutions

• Three laws of thermodynamics
  1. The energy of the universe is constant
  2. In any spontaneous process, there is always an increase in the entropy of the universe.
  3. The entropy of a perfect crystal at 0°C K is zero
Brief Review of Relevant Thermodynamic Concepts

• **Chemical Thermodynamics:** Yields information on the tendency of reactions to occur under conditions of known system composition, temperature and pressure.

• Important concept is the Gibbs **free energy change** ($\Delta G_r$) associated with a reaction:

• Related to:
  - 1. activity or chemical potential of a substance
  - 2. the energy of formation of a compound
  - 3. the equilibrium constant of a reaction
  - 4. the electrode potential potential for a system.
The Equilibrium Condition

- For a system at constant T and P, the equilibrium condition states:
  \[ \Delta G_r = \Delta G_{\text{products}} - \Delta G_{\text{reactants}} \]

- \( G \): Gibbs free energy is related to enthalpy and entropy by: \( G = H - TS \)

- When the temperature of the products and reactants are equal, the change in Gibbs free energy is given by:
  \[ \Delta G_r = \Delta H_r - T\Delta S_r \]

- \( G, H, \) and \( S \) are state variables of a system that change as a result of chemical processes.

- Depend only on the state of the system and not on how system arrived at that state.
Gibbs Free Energy of Reaction ($G_r$)

- $G$ = Gibbs free energy
- $\Delta G_r$ is the energy obtainable from a reaction [kJ mol$^{-1}$]
- $\Delta G_r < 0$: reactant $\rightarrow$ product is thermodynamically spontaneous.
- $\Delta G_r > 0$: product $\rightarrow$ reactant is thermodynamically spontaneous.
- $\Delta G_r = 0$: reactant $\leftrightarrow$ product are in equilibrium
Free energy change of a reaction

- Change in free energy of a reaction at standard conditions \((T = 298\, K, P = 0.1\, \text{MPa}, a_i = 1)\):

\[ \Delta G^0_r = \sum (\Delta G_f \text{ products}) - \sum (\Delta G_f \text{ reactants}) \]

- \(\Delta G_f\) values are tabulated for most compounds.
Relationship between $\Delta G_r$, $\Delta G^0_r$, and $K$:

$$\Delta G_r = \Delta G^0_r + RT \ln Q$$

$\Delta G_r$ is free energy change for given set of conditions

$R$ = molar gas constant (8.314 J K$^{-1}$ mol$^{-1}$)

At equilibrium $Q = K$ and

$$\Delta G_r = 0 = \Delta G^0_r + RT \ln K,$$

$$\Delta G^0_r = -RT \ln K \quad (RT = 2.48 \text{ kJ mol}^{-1} \text{ at } 298.2\text{K})$$

Thus, if we know $\Delta G_f$ for reactants and products in a reaction,

- we can find $\Delta G^0_r$ for reaction

- then can determine $K$
Thermodynamics of Redox

- The e-'s represent a common currency for examining conditions of thermodynamic spontaneity and equilibrium when comparing reactions.
- The thermodynamic spontaneity of the reaction is determined by the potential for e- to be transferred in one direction or another.
Oxidation-Reduction Reactions

- A redox reaction involves the transfer of one or more electrons (e\(^-\)) from one species to another.

\[
\text{Reduced Species A} + \text{Oxidized Species B} \rightleftharpoons \text{Oxidized Species A} + \text{Reduced Species B}
\]

- The reaction proceeds in either direction, depending on magnitude and sign of \(\Delta G_r\).
The full redox reaction:

\[
\text{Reduced Species A} + \text{Oxidized Species B} \leftrightarrow \text{Oxidized Species A} + \text{Reduced Species B}
\]

contains two half reactions, where each pertains to a given element that undergoes oxidation or reduction:

\[
\text{Red A} \leftrightarrow \text{Ox A} + m \text{ H}^+ (aq) + e^- (aq)
\]

\[
\text{Ox B} + m \text{ H}^+ (aq) + e^- (aq) \leftrightarrow \text{Red B}
\]
Electrochemical Cell

$H_2 = 1 \text{ atm}$

$\frac{1}{2}H_2(g) \leftrightarrow H^+ + e^-$

$a_{H^+} = 1$

$Fe^{3+} + e^- \leftrightarrow Fe^{2+}$
<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E^0_{\text{H}}$</th>
<th>log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) $\frac{1}{4}$ $O_2 (g) + H^+ (aq) + e^- (aq) = \frac{1}{2} H_2O (l)$</td>
<td>1.22</td>
<td>20.8</td>
</tr>
<tr>
<td>(2) $1/5$ NO$_3^-$ (aq) + $6/5$ H$^+$ (aq) + e$^-$ (aq) = $1/10$ N$_2$ (g) + $3/5$ H$_2$O (l)</td>
<td>1.24</td>
<td>21.0</td>
</tr>
<tr>
<td>(3) $\frac{1}{2}$ MnO$_2$ (s) + 2 H$^+$ (aq) + e$^-$ (aq) = $\frac{1}{2}$ Mn$^{2+}$ (aq) + H$_2$O (l)</td>
<td>1.23</td>
<td>20.8</td>
</tr>
<tr>
<td>(4) $\frac{1}{2}$ NO$_3^-$ (aq) + H$^+$ (aq) + e$^-$ (aq) = $\frac{1}{2}$ NO$_2^-$ (aq) + $\frac{1}{2}$ H$_2$O (l)</td>
<td>0.835</td>
<td>14.2</td>
</tr>
<tr>
<td>(5) Fe(OH)$_3$ (s) + 3 H$^+$ (aq) + e$^-$ (aq) = Fe$^{2+}$ (aq) + 3 H$_2$O (l)</td>
<td>1.06</td>
<td>18.0</td>
</tr>
<tr>
<td>(6) Fe$^{3+}$ (aq) + e$^-$ (aq) = Fe$^{2+}$ (aq)</td>
<td>0.711</td>
<td>12.1</td>
</tr>
<tr>
<td>(7) $\frac{1}{2}$ $O_2 (g) + H^+ (aq) + e^- (aq) = \frac{1}{2} H_2O_2 (aq)$</td>
<td>0.682</td>
<td>11.6</td>
</tr>
<tr>
<td>(8) $1/8$ SO$_4^{2-}$ (aq) + $5/4$ H$^+$ (aq) + e$^-$ (aq) = $1/8$ H$_2$S (g) + $\frac{1}{2}$ H$_2$O (l)</td>
<td>0.303</td>
<td>5.14</td>
</tr>
<tr>
<td>(9) $\frac{1}{2}$ CH$_2$O (aq) + H$^+$ (aq) + e$^-$ (aq) = $\frac{1}{2}$ CH$_3$OH (aq)</td>
<td>0.235</td>
<td>3.98</td>
</tr>
<tr>
<td>(10) $\frac{1}{4}$ CH$_2$O (aq) + H$^+$ (aq) + e$^-$ (aq) = $1/4$ CH$_4$ (aq)</td>
<td>0.409</td>
<td>6.93</td>
</tr>
<tr>
<td>(11) $1/8$ CO$_2$ (g) + H$^+$ (aq) + e$^-$ (aq) = $1/8$ CH$_4$ (g) + $\frac{1}{4}$ H$_2$O (l)</td>
<td>0.169</td>
<td>2.86</td>
</tr>
<tr>
<td>(12) H$^+$ (aq) + e$^-$ (aq) = $\frac{1}{2}$ H$_2$ (g)</td>
<td>0.00</td>
<td>0.0</td>
</tr>
<tr>
<td>(13) $1/4$ CO$_2$ (g) + H$^+$ (aq) + e$^-$ (aq) = $\frac{1}{4}$ CH$_2$O (g) + $\frac{1}{4}$ H$_2$O (l)</td>
<td>-0.071</td>
<td>-1.20</td>
</tr>
</tbody>
</table>
FIGURE 9-2
Eh-pH diagram for the simple ions of iron at 25°C and 1 bar. The dashed lines denote Eh and pH conditions for equal activities of the aqueous species. Lines marked A, B, and C represent equal activities of iron species determined from Eq. (9-11), (2-27), and (9-42), respectively. Redox potential is expressed as volts (Eh) on the left side and as pe on the right side. (Reprinted by permission from Nordstrom and Munoz, 1985.)
Overall redox reaction in soil is sum of two half-reactions

\[
\text{Fe(OH)}_3(s) + 3\text{H}^+(aq) + e^- \leftrightarrow \text{Fe}^{2+} (aq) + 3\text{H}_2\text{O (l)}; \quad \log K = 18.0
\]

- is a reduction half-reaction.
- This reaction must be combined (coupled) with another half-reaction that is inverted to represent an oxidation half-reaction.
- No free electrons appear in balanced full redox reactions.
- For example, the reduction of Mn(IV) to Mn (II) could be coupled with the oxidation of CH\(_2\)O to CO\(_2\) as indicated in the Table.
Summing two half reactions (e.g., dissimilatory Fe reduction)

Fe(OH)$_3$(s) + 3 H$^+$ + e$^-$ $\leftrightarrow$ Fe$^{2+}$ + 3 H$_2$O $\quad$ log K = 18.0

$\frac{1}{4}$ CH$_2$O + $\frac{1}{4}$ H$_2$O $\leftrightarrow$ $\frac{1}{4}$ CO$_2$(g) + H$^+$ + e$^-$ $\quad$ log K = 1.2

Fe(OH)$_3$(s) + $\frac{1}{4}$ CH$_2$O + 2 H$^+$ + $\leftrightarrow$ Fe$^{2+}$ + $\frac{1}{4}$ CO$_2$ + 2.75 H$_2$O $\quad$ log K = 19.2

Will this reaction proceed under standard conditions?

How about under non-std. conditions when activities of reactants and products not = 1?
Table 8.8. Sequence of Progressive Reduction of Redox Intensity by Organic Pollutants

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Chemical Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂ consumption (respiration)</td>
<td>[ \frac{1}{4} { \text{CH}_2\text{O} } + \frac{1}{4} \text{O}_2 = \frac{1}{4} \text{CO}_2 + \frac{1}{4} \text{H}_2\text{O} ]</td>
</tr>
<tr>
<td>Denitrification</td>
<td>[ \frac{1}{4} { \text{CH}_2\text{O} } + \frac{1}{3} \text{NO}_3^- + \frac{1}{3} \text{H}^+ = \frac{1}{4} \text{CO}_2 + \frac{1}{10} \text{N}_2 + \frac{1}{2} \text{H}_2\text{O} ]</td>
</tr>
<tr>
<td>Nitrate reduction</td>
<td>[ \frac{1}{4} { \text{CH}_2\text{O} } + \frac{1}{8} \text{NO}_3^- + \frac{1}{4} \text{H}^+ = \frac{1}{4} \text{CO}_2 + \frac{1}{8} \text{NH}_4^+ + \frac{1}{8} \text{H}_2\text{O} ]</td>
</tr>
<tr>
<td>Production of soluble Mn(II)</td>
<td>[ \frac{1}{4} { \text{CH}_2\text{O} } + \frac{1}{2} \text{MnO}_2(\text{s}) + \text{H}^+ = \frac{1}{4} \text{CO}_2 + \frac{1}{2} \text{Mn}^{2+} + \frac{1}{8} \text{H}_2\text{O} ]</td>
</tr>
<tr>
<td>Fermentation</td>
<td>[ \frac{3}{4} { \text{CH}_2\text{O} } + \frac{1}{4} \text{H}_2\text{O} = \frac{1}{4} \text{CO}_2 + \frac{1}{2} \text{CH}_3\text{OH} ]</td>
</tr>
<tr>
<td>Production of soluble Fe(II)</td>
<td>[ \frac{1}{4} { \text{CH}_2\text{O} } + \text{FeOOH}(\text{s}) + 2\text{H}^+ = \frac{1}{4} \text{CO}_2 + \frac{7}{4} \text{H}_2\text{O} + \text{Fe}^{2+} ]</td>
</tr>
<tr>
<td>Sulfate reduction, production of H₂S</td>
<td>[ \frac{1}{4} { \text{CH}_2\text{O} } + \frac{1}{8} \text{SO}_4^{2-} + \frac{1}{8} \text{H}^+ = \frac{1}{8} \text{HS}^- + \frac{1}{4} \text{CO}_2 + \frac{1}{4} \text{H}_2\text{O} ]</td>
</tr>
<tr>
<td>Methane fermentation</td>
<td>[ \frac{1}{4} { \text{CH}_2\text{O} } = \frac{1}{8} \text{CH}_4 + \frac{1}{8} \text{CO}_2 ]</td>
</tr>
</tbody>
</table>
Sequence of TEAPs is consistent with the decrease in energy yield per mole of organic matter oxidized.
Figure 5-3. Sequence in time of transformations in soil after flooding, beginning with oxygen depletion and followed by nitrate and then sulfate reduction. Increases are seen in reduced manganese, reduced iron, hydrogen sulfide, and methane. Note the gradual decrease in organic substrate (electron donor) and increases in available ammonium and phosphate ions. Graph can also be interpreted as relative concentrations with depth in wetland soils. (By K. R. Reddy, University of Florida, Gainesville; reprinted with permission)
(c) Biogeochemical redox = the energy economy

O₂ → H₂O → NO₃⁻ → N₂ → Fe(III) → Fe(II) → SO₄²⁻ → H₂S → Organic C → CO₂

Decreasing energy yield

Burgin et al 2011