ESM 202

Water Quality: Additional concepts

Alkalinity

- Alkalinity is a measure of the Acid Neutralizing Capacity (ANC) of an aqueous body (lake, ocean, stream, groundwater)
- Where does it come from:
  - 
  - 
- What does it mean?

Carbonate System

- Carbonic acid is formed after CO₂ dissolves in water:
  \[
  \begin{align*}
  \text{CO}_2(\text{g}) & \leftrightarrow \text{CO}_2(\text{aq}) \\
  \text{CO}_2(\text{aq}) + \text{H}_2\text{O} & \leftrightarrow \text{H}_2\text{CO}_3
  \end{align*}
  \]
  \[p_{K_{\text{H}}} = 1.5\]
- Carbonic acid can lose up to 2 H⁺
  \[
  \begin{align*}
  \text{H}_2\text{CO}_3 & \leftrightarrow \text{HCO}_3^- + \text{H}^+ \\
  \text{HCO}_3^- & \leftrightarrow \text{CO}_3^{2-} + \text{H}^+
  \end{align*}
  \]
  \[p_{K_1} = 6.3, \quad p_{K_2} = 10.3\]

Carbonate System

- Minerals with carbonate
  - Limestone/calcite: CaCO₃ ⇌ Ca²⁺ + CO₃²⁻
  - Dolomite: MgCO₃ ⇌ Mg²⁺ + CO₃²⁻
  - FeCO₃ ⇌ Fe²⁺ + CO₃²⁻
- Dissolved concentration of Ca²⁺, Mg²⁺ and Fe²⁺ is controlled by pH and [CO₃²⁻]

Dissolved Carbon Dioxide: Closed System

- Start with a closed system
  - groundwater situation where carbonate rocks (limestone, dolomite) are present, but there is no contact with atmosphere
Dissolved Carbon Dioxide: Closed System

- In a closed system
  - total concentration of carbonate is constant
  \[ C_{\text{tot}} = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = \text{DIC} \]
  - DIC = Dissolved Inorganic Carbon
  - A typical value is \( C_{\text{tot}} = 10^{-3} \text{ mol/L} \)
    \[ \text{pC}_{\text{tot}} = 3 \]

Dissolved Carbon Dioxide: Open System

- Concentration of CO2 in the atmosphere
  - \( \sim 380 \text{ ppmv} \Rightarrow P_{\text{CO}_2} = 10^{-3.5} \text{ atm} \)
  - relatively constant
- Since \( P_{\text{CO}_2} \) is \( \sim \) constant and \( K_H \) is constant
  - \([\text{H}_2\text{CO}_3]\) is constant
  - independent of pH
  \[ [\text{H}_2\text{CO}_3] = P_{\text{CO}_2} \cdot K_{H,\text{CO}_2} = 10^{-3.5} \cdot 10^{-1.5} = 10^{-5} \text{ M} \]
  \[ \text{pH}_{\text{CO}_3} = 5 \]

Carbonate System

- Take home message:
  - Type of inorganic carbon depends on pH
  - Low pH \( \Rightarrow \) carbonic acid
  - Mid pH \( \Rightarrow \) bicarbonate
  - High pH \( \Rightarrow \) carbonate
  - Depends on whether system is open or closed
  - Has major influence on alkalinity, buffering capacity and hardness

Alkalinity

- Alkalinity
  - capacity of water to accept \( \text{H}^+ \)
  - sum of chemical species that accept \( \text{H}^+ \) in water:
    \[ \text{Alkalinity} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] + [\text{B(OH)}_4^-] + [\text{NH}_3] + [\text{HS}^-] + ... \]
  - In many cases we refer to only the carbonate components of alkalinity, since these are the major constituents:
    \[ \text{Alk} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \]
Effect of Photosynthesis

- For example, the uptake of NH$_4^+$ results in the release of H$, affecting alkalinity and pH
  
  
  
  $106 \text{ CO}_2 + 16 \text{ NH}_4^+ + \text{ HPO}_4^{2-} + 108 \text{ H}_2\text{O}$
  
  $\rightarrow (\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}\text{PO}_4 + 107 \text{ O}_2 + 14 \text{ H}^+$

- If NO$_3^-$ is used to produce algae, then H$^+$ are needed, increasing pH and affecting alkalinity

  $106 \text{ CO}_2 + 16 \text{ NO}_3^- + \text{ HPO}_4^{2-} + 122 \text{ H}_2\text{O}$

  $+ 18 \text{ H}^+ = (\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}\text{PO}_4 + 138 \text{ O}_2$

Buffer Capacity

- An aqueous solution is “buffered” when the concentration of dissolved ions is relatively large
  
  - Addition of small amounts of strong acids or bases does not change the pH of solution significantly
  - Highest buffering near pK$_1$ and pK$_2$
  - Ocean is very well buffered

Oceanic carbon

- Oceanic carbon is present in four major forms:
  
  - DIC = 37,500 Pg C $\approx 2.25 \times 10^{-3}$ mol/L
  
  - DOC = Dissolved Organic Carbon = 1,000 Pg C $\approx 0.06$ mM
  
  - POC = Particulate Organic Carbon = 30 Pg C $\approx 0.002$ mM

- Marine biota (microorganisms, plants and animals)
**Oceanic carbon**

- Organic acids in DOC are considered as:
  \[ H(\text{DOC}) = \text{DOC}^- + H^+ \quad pK_{\text{DOC}} \approx 5.5 \]

- Marine biota are only \( \sim 3 \) Pg (0.0002 mM)
  - Large impact on cycling of carbon and nutrients
  - Can have significant effect on alkalinity

**Redox Potential**

**Redox Conditions**

- **What are Redox Conditions?**
  - Determine whether local environment is
    - Oxidative
    - Reducing
  - Gradient of conditions
    - Atmosphere is highly oxidative
    - Deep sediments are highly reducing
- **How do we measure redox conditions?**
  - Concentration of available electrons for transfers: \( pe = -\log[e^-] \)

**Why do we care?**

- Determines the form in which an element will be present
  - Oxidized (e.g. \( \text{CO}_2, \text{CO}, \text{NO}_3^-, \text{SO}_4^{2-}, \text{Fe}^{3+} \))
  - Reduced (e.g. \( \text{CH}_4, \text{NH}_3, \text{H}_2\text{S}, \text{Fe}^{2+} \))
- Availability & toxicity of element depends on form
  - \( \text{Cr}^{3+} \) vs. \( \text{Cr}^{6+} \)
  - \( \text{Hg}^{(0)} \) vs. \( \text{Hg}^+ \)
- Energy stored in reduced forms

**Quick Review of Oxidation States**

- Only a few elements (C, N, O, S, Fe, Mn) participate significantly in natural redox processes
- As a rule, molecules of the element itself (e.g. \( \text{N}_2, \text{O}_2, \text{H}_2, \text{Fe}, \text{Pb} \)) are in a “zero” oxidation state.
- Some elements have in general only one other oxidation state:
  - H is always +1
  - O is usually -2
  - Halogens (Cl, Br, I, F) are usually -1

Example: Carbon (C) goes from -4 to +4

- CH\(_3\) \(-4\) \( \rightarrow \) CH\(_2\)=CH\(_2\) \(-2\) \( \rightarrow \) CH\(_2\)O \(+2\) \( \rightarrow \) CO\(_2\) \(+4\)

**Example: Nitrogen (N) goes from -3 to +5**

- NH\(_3\) \(-3\) \( \rightarrow \) N\(_2\) \(+0\) \( \rightarrow \) N\(_2\)O \(+1\) \( \rightarrow \) NO\(_2\) \(+4\) \( \rightarrow \) NO\(_3^-\) \(+5\)

100% reduced \( \longleftrightarrow \) 100% oxidized
Minerals (Inorganic Ions)

- Common Anions:
  - F\(^-,\) Cl\(^-,\) Br\(^-,\) I\(^-,\) OH\(^-,\) NO\(_2^-,\) NO\(_3^-,\) SO\(_4^{2-},\) HS\(^-,\) S\(^2-,\) HCO\(_3^-,\) CO\(_3^{2-},\) PO\(_4^{3-},\) HPO\(_4^{2-}\)

- Common Cations:
  - NH\(_4^+,\) Ca\(^{2+},\) Mg\(^{2+},\) Fe\(^{2+},\) Fe\(^{3+},\) Na\(^+,\) K\(^+,\) H\(^+\)

- Less common ions:
  - Pb\(^{2+},\) Cd\(^{2+},\) Zn\(^{2+},\) Hg\(^+,\) Hg\(^{2+},\) Cr\(^{3+}\)

What are common redox conditions?

Redox Potential

- Examples of common oxidation/reduction reactions
  - \(4Fe + 3O_2 \rightarrow 2Fe_2O_3\) (chemical)
  - \(Fe^{2+} \rightarrow Fe^{3+} + e^-\) (biochemical)
  - \(CO_2(g) + 8H^+ + 8e^- \rightarrow CH_4(g) + 2H_2O\) (biological)
  - \(C_6H_5O_7^{2-} + 6H_2O \rightarrow 6CO_2(g) + 24H^+ + 24e^-\) (biochemical)

- Energy is associated with these electron transfers

Redox

- Every oxidation reaction is coupled with a reduction reaction:
  - \(4Fe^{2+} = 4Fe^{3+} + 4e^-\) (oxidation)
  - \(O_2 + 4H^+ + 4e^- = 2H_2O\) (reduction)
  - \(O_2 + 4H^+ + 4Fe^{2+} = 2H_2O + 4Fe^{3+}\)

- Thermodynamic Sequence of Reduction

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(E_h (V))</th>
<th>(\Delta G (kcal/mol e^-))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduction of (O_2)</td>
<td>(O_2 + 4H^+ + 4e^- \rightarrow 2H_2O)</td>
<td>(0.812)</td>
</tr>
<tr>
<td>Reduction of (NO_2^-)</td>
<td>(NO_2^- + H_2O + e^- \rightarrow NO_3^- + H_2O)</td>
<td>(0.747)</td>
</tr>
<tr>
<td>Reduction of (Mn^{4+}) to (Mn^{2+})</td>
<td>(MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O)</td>
<td>(0.526)</td>
</tr>
<tr>
<td>Reduction of (Fe^{3+}) to (Fe^{2+})</td>
<td>(Fe(OH)_3 + 3H^+ + e^- \rightarrow Fe^{2+} + 3H_2O)</td>
<td>(-0.047)</td>
</tr>
<tr>
<td>Reduction of (SO_4^{2-}) to (H_2S)</td>
<td>(SO_4^{2-} + 10H^+ + 8e^- \rightarrow H_2S + 4H_2O)</td>
<td>(-0.221)</td>
</tr>
<tr>
<td>Reduction of (CO_2) to (CH_4)</td>
<td>(CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O)</td>
<td>(-0.244)</td>
</tr>
</tbody>
</table>

Assuming coupling to the oxidation of organic matter:

- \(\frac{1}{4}CH_4O + \frac{1}{4}H_2O = \frac{1}{4}CO_2(g) + H^+ + e^-\)
**Redox Potential**

- Concentration gradient of O₂: top layers oxic and the bottom anoxic
- Diffusion of O₂ from the surface of the water to the deeper layers is **slow**
- Many organisms make use of the available O₂ as it diffuses downward
- Reduction occurs in the anoxic environment (low redox potential)

**Sequence of Redox Conditions**

- **Aerobic**
  - Atmosphere
  - Aerobic, O₂ based
  - Aerobic, O₂ or NO₃⁻ → NH₄⁺
- **Facultative Anaerobic**
  - Surface water
  - Facultative Anaerobic, O₂ or NO₃⁻ → NH₄⁺
- **Anaerobic**
  - Mn⁴⁺ or Fe³⁺ → Mn²⁺ or Fe²⁺
  - Anaerobic, SO₄²⁻ → H₂S, HS⁻
  - Anaerobic, CO₂ → CH₄

**Redox**

- Reducing (low pe)
- Oxidizing (high pe)

**Redox**

- pC-pe Diagram for the NO₃⁻/NH₄⁺ System at pH 7

**Redox**

- pC-pe Diagram for the Fe³⁺/Fe²⁺ System at Low pH

**Redox**

- pC-pe Diagram for the Fe⁺⁺/Fe⁺³ System at pH
Kinetics: Rate of Reaction

Rate of Reaction

- Overall rate of reaction
  - May be controlled by mixing
  - Availability for reacting

- In some cases, rate of reaction depends only on concentration of reactants:

\[
A + B = C + D
\]

\[
\frac{d[A]}{dt} = \frac{d[B]}{dt} = -k[A][B] = -\frac{d[C]}{dt} = -\frac{d[D]}{dt}
\]

Rate of Reaction

- Example:
  - oxidation of CH₄ in the atmosphere

\[
CH₄ + OH \rightarrow CH₃ + H₂O
\]

\[
\frac{d[CH₄]}{dt} = -k[CH₄][OH⁺]
\]

Rate of Reaction

- In other conditions, one of the reactants is abundant, so the reaction is independent of it:

\[
\frac{d[CH₄]}{dt} = -k[CH₄]
\]

This is the case for methanothrophic conversion of CH₄ to CH₃OH by bacteria

- Other reactions can be quite a bit more complex:

\[
\frac{d[Fe^{2+}]}{dt} = -k[Fe^{2+}][OH^-]P_{o₂}
\]

Aquatic Chemistry

- Thermodynamics:
  - determine how various chemical components in environment will behave
  - under a given set of conditions (e.g. pH, pe, T)

- Kinetics
  - understand rates at which these processes (reactions) can occur
  - understand how can they be accelerated by biotic activity
Key Points on Water Quality

- Diversity of indicators of WQ
- Dissolution of gases: controlled by Henry's Law ($K_H$)
- Dissociation of acids & bases: controlled by $K_A$ or $K_B$
- pH controls whether chemical is present as acid, base or dissociated
- Important systems: Carbonate, Nitrate, Ammonia and Phosphate
- Alkalinity: capacity to neutralize acid
- Redox: oxidizing vs. reducing conditions
  - Controlled by $p_e$
  - Availability of oxygen
- Kinetics: equilibrium can take time...