Chapter 7
Ocean Chemistry

About solutions and mixtures

A solution is made of two components, with uniform (meaning 'the same everywhere') molecular properties:

The solvent, which is usually a liquid, and is the more abundant component.

The solute, often a solid or gas, is the less abundant component.

A mixture is different from a solution. In a mixture the components retain separate identities, so it is NOT uniform throughout.

Water is a powerful solvent and we have it everywhere – the hydrological cycle

Ocean Salinity

- **Salinity** is the total quantity of dissolved inorganic solids in water.
- 3.5% salt on average
- measured in g/kg (ppt = parts per thousand)

Ocean salinities vary in space

Processes that affect salinity: evaporation, precipitation, runoff, freezing, and thawing

And recall that:
- The heat capacity of water decreases with increasing salinity
- As salinity increases, freezing point decreases
- As salinity increases, evaporation slows (boiling point increases)

Ocean-Surface Conditions Depend on Latitude, Temperature, and Salinity

Mid Ocean Average Surface Salinity

Surface Salinity Northern Hemisphere Summer
• Dissolved salts
  - Salts have ionic bonds
    - e- transferred from metal to non-metal
    - Ions of opposite charge are created
    - Attraction forms an ionic bond
    - Ionic bonds are easily broken
    - Salts break apart (dissociate) into ions in water
    - i.e. NaCl

One kilogram of seawater
Water 965.6 g
Other components (salinity) 34.4 g

Sources of salt:
- Positive ions: weathering and erosion
- Negative ions: gases from volcanic eruptions
- Hydrothermal activity supply and remove salt from the deep ocean

Balance of salt:
Input: rivers, volcanic activity, groundwater, hydrothermal vents and cold springs, and the decay of once-living organisms.
Output: sea spray, uptake by living organisms, incorporation into sediments, and ultimately by subduction.

Regulating the major constituents in seawater

Residence time: the average time a substance remains in solution in the ocean
- Total amount divided by rate of input (or output)

### Table 7.1: Major Constituents of Seawater at 34.4% Salinity

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Concentration in Parts per Thousand (% of Total)</th>
<th>Percent by Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water H₂O</td>
<td>89.8</td>
<td>96.5</td>
</tr>
<tr>
<td>Most Major Ions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium (Na⁺)</td>
<td>10.556</td>
<td>10.7</td>
</tr>
<tr>
<td>Chloride (Cl⁻)</td>
<td>18.980</td>
<td>20.2</td>
</tr>
<tr>
<td>Magnesium (Mg²⁺)</td>
<td>1.272</td>
<td>1.46</td>
</tr>
<tr>
<td>Calcium (Ca²⁺)</td>
<td>0.400</td>
<td>0.45</td>
</tr>
<tr>
<td>Potassium (K⁺)</td>
<td>0.380</td>
<td>0.41</td>
</tr>
<tr>
<td>Sulfate (SO₄²⁻)</td>
<td>2.649</td>
<td>2.80</td>
</tr>
<tr>
<td>Bicarbonate (HCO₃⁻)</td>
<td>0.140</td>
<td>0.15</td>
</tr>
<tr>
<td>Sulfate (SO₄²⁻)</td>
<td>2.649</td>
<td>2.80</td>
</tr>
<tr>
<td>Total</td>
<td>999.377</td>
<td>100.0</td>
</tr>
</tbody>
</table>

See Table 7.2 for minor and trace elements in seawater

### Table 6.3: Approximate Residence Time of Ions in the Oceans

<table>
<thead>
<tr>
<th>Ion</th>
<th>Time in Years</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride</td>
<td>100 million</td>
</tr>
<tr>
<td>Sodium</td>
<td>210 million</td>
</tr>
<tr>
<td>Magnesium</td>
<td>22 million</td>
</tr>
<tr>
<td>Potassium</td>
<td>11 million</td>
</tr>
<tr>
<td>Sulfate</td>
<td>11 million</td>
</tr>
<tr>
<td>Calcium</td>
<td>1 million</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.0014 million</td>
</tr>
<tr>
<td>Iron</td>
<td>0.00014 million</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.000013 million</td>
</tr>
</tbody>
</table>

The ratio of dissolved solids in the ocean is constant:

- Well-mixed solution
- Principle of Constant Proportions: the ratios between the concentrations of major conservative ions in open-ocean water are constant

Seawater's constituents may be conservative or nonconservative

- Conservative = concentration changes only as a result of mixing, diffusion, and advection
- Non-conservative = concentration changes as a result of biological or chemical processes as well as mixing, diffusion, and advection

The ocean is in chemical equilibrium

- Salt composition constant for last 1.5 billion years
  - $5 \times 10^{22} \text{g} =$ total dissolved material
  - $2.5 \times 10^{15} \text{g} =$ total run off per year
  - Salinity is not increasing!
  - Therefore: rate of addition ~ rate of removal

Determining salinity:

- Electrical conductivity is a function of salinity
- More ions = greater transmission of electricity

Gases

- Distribution with depth
  - Photosynthesis removes $\text{CO}_2$ and produces $\text{O}_2$ at the surface
  - Respiration produces $\text{CO}_2$ and removes $\text{O}_2$ at all depths
  - Compensation depth (Photosynthesis = Respiration)

Oxygen and $\text{CO}_2$ profiles

- $\text{O}_2$ Concentrations
  - Photosynthesis
  - Bottom water enrichment

- $\text{CO}_2$ Concentrations
  - Direct solution of gas from the atmosphere
  - Respiration of marine organisms
  - Oxidation (decomposition) of organic matter
The Carbon/Carbon Dioxide Cycle -
- Ocean uptake from atmosphere
  Depends on: pH, temperature, salinity, chemistry
- Biological pump

Numbers in black = rates of exchange
Numbers in green = total amounts stored in reservoirs
Numbers in parenthesis = net annual changes

Ocean uptake from atmosphere
Depends on: pH, temperature, salinity, chemistry

Biological pump

Some words to keep in mind:
- Ion – charged atom
cat-ion (+) – positively charged ion
an-ion (-) – negatively charged ion

Dissociation = to break apart into ions

H₂O \[\text{OH}^-\] \[\text{H}^+\]

Pure Water: \([\text{OH}^-]=10^{-7}\) \([\text{H}^+]=10^{-7}\)
Neutral solution: \([\text{H}^+]=[\text{OH}^-]\)

(all 3 will be in water solutions)

Other Substances
- Nutrients
  - Ions required for plant growth
  - Redfield ratios
  - Nutrient cycles
- Organics
  - Wide variety of substances
    - Some are oxidized or broken down into smaller molecules
    - Some accumulate in the sediment to form oil and gas deposits

Non-pure water solutions
- \([\text{OH}^-]\) and \([\text{H}^+]\) are inversely proportional
- Imbalance between the relative concentration of \([\text{H}^+]\) and \([\text{OH}^-]\) produces an acidic or basic solution
- pH scale - measures acidity/alkalinity
  - 0-14
  - Logarithmic scale: \(pH=-\log_{10}[10^{-5}]=5\)
  - pH of rainwater ~ 5-6 (on the acidic side)

### Table 6.6: Nutrients in Seawater

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration μg/kg</th>
<th>Relative Molar Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen (N)</td>
<td>500</td>
<td>16</td>
</tr>
<tr>
<td>Phosphorus (P)</td>
<td>70</td>
<td>1</td>
</tr>
<tr>
<td>Silicon (Si)</td>
<td>3000</td>
<td>40</td>
</tr>
</tbody>
</table>

1. Parts per billion.
Seawater

- Alkaline, pH from 7.5-8.5
- Average pH=7.8
- pH relatively constant due to buffering action of CO₂

Buffer = substance that prevents sudden or large changes in the acidity or alkalinity of a solution
- Important for biological processes
- pH inversely proportional to the concentration of CO₂

CO₂ combines readily with seawater to form carbonic acid (H₂CO₃). Carbonic acid can then lose a H⁺ ion to become a bicarbonate ion (HCO₃⁻), or two H⁺ ions to become a carbonate ion (CO₃²⁻). Some bicarbonate ions dissociate to form carbonate ions, which combine with calcium ions in seawater to form calcium carbonate (CaCO₃), used by some organisms to form hard shells and skeletons. When their builders die, these structures may fall to the seabed as carbonate sediments, eventually to be redissolved. As the double arrows indicate, all these reactions may move in either direction.

Chapter 7 - Summary

- pH: acidity of seawater 7.5 - 8.5
- Carbon dioxide acts as a buffer that prevents large variations in pH
- Major salt ions are in constant proportions except in coastal areas
- Ocean is a net source of oxygen to atmosphere
- Biological processes pump CO₂ into the deep ocean

Chapter 7 - Summary

- The polar nature of the water molecule is responsible for water’s remarkable ability to dissolve more substances than any other natural solvent.
- The most abundant ions dissolved in seawater are chloride, sodium, sulfate.
- The quantity of dissolved inorganic solids in water is its salinity.
- Though most solids and gases are soluble in water, the ocean is in chemical equilibrium, and neither the proportion nor the amount of most dissolved substances changes significantly through time.
- Nitrogen is the most abundant dissolved gas in seawater; oxygen is the second most abundant. Carbon dioxide is the most soluble gas, and one of many substances that affect the ocean’s pH balance.
- Seawater acts as a buffer to prevent broad swings of pH when acids or bases are introduced.

Good Stuff

1. Calculate the residence time of water in the oceans.
2. How many times could a water molecule have been recycled since the formation of the oceans?