Dissolved Gases other than Carbon Dioxide in Seawater

OCN 623 – Chemical Oceanography

29 January 2013

Reading: Libes, Chapter 6 – pp. 147-158
Outline

1. Basic concepts
   • Gas laws
   • Gas solubility and air-sea equilibrium

2. Dissolved oxygen variability in the ocean

3. “Unusual” gases in the ocean
   • Hydrogen sulfide
   • Methane hydrates
**Fundamental Gas Laws**

1) \( C_G = [G] \) = gas concentration (mole/L) of gas “G” in solution

2) \( p_G \) = partial pressure (atm or kPa) of gas “G” in a gas mixture or a liquid

3) \( P_{Total} = P_{N_2} + P_{O_2} + P_{Ar} + P_{H_2O} + \ldots \) (in gas phase) (Dalton’s Law)

\[
P_G = P_{Total} \cdot (\text{mole fraction of “G” in a gas mixture})
\]

In the atmosphere (at 1 atm TOTAL pressure and 100% relative humidity):

\[
\begin{align*}
P_{N_2} &= 0.78 \text{ atm} & P_{CO_2} &= 0.00038 \text{ atm} \\
P_{O_2} &= 0.21 \text{ atm} & P_{CH_4} &= 0.0000014 \text{ atm}
\end{align*}
\]
4) IDEAL GAS LAW: \( P_{\text{Total}} V = nRT \)
   \( (T = ^\circ\text{K}, \; n = \# \text{ of moles}, \; V = \text{volume}, \; R = \text{ideal gas constant}) \)

   AT STP \((0^\circ\text{C}, 1\text{atm})\) in the gaseous state:
   
   \( 1 \text{ mole} = 22.4 \text{ L} \)

5) HENRY’S LAW: \( P_G = K_G \cdot C_G \) (under equilibrium conditions)

   \( K_G = \text{“Henry’s Law Constant”} \) (a function of S and T)

   \( 1/K_G = \beta_G = \text{“Bunsen Coefficient”} = \text{Amount of gas which can be dissolved in a unit of volume of water at a given T and S, when P_G is given (assume 1atm if not stipulated) } \) 

   Units: \( \frac{\text{mL (or moles)_GAS}}{\text{L}_\text{sw} \cdot \text{atm}} \)
6) **Setchenow Relationship** ("Salting-out Effect"):

\[
\ln \beta = b_1 + (b_2 \cdot S)
\]

where \( b_1 \) and \( b_2 \) are constants for each gas for a given temp.

- Lower salinity corresponds to higher solubility

7) **Effect Of Salinity And Temperature**:

\[
\ln C_G = A_1 + A_2 \left( \frac{100}{T} \right) + A_3 \ln \left( \frac{T}{100} \right) + A_4 \left( \frac{T}{100} \right) + S \left[ B_1 + B_2 \left( \frac{T}{100} \right) + B_3 \left( \frac{T}{100} \right)^2 \right]
\]

\( T = ^\circ K \) \hspace{1cm} \( S = \) salinity \hspace{1cm} (Weiss, 1970)

- Lower temp corresponds to higher solubility

Constants are quoted for a given \( p_{Tot} \) (e.g., Table 8.3)
Gas Solubility - Empirical Data

\[ \ln C_G = A_1 + A_2 \left( \frac{100}{T} \right) + A_3 \ln \left( \frac{T}{100} \right) + A_4 \left( \frac{T}{100} \right) + S \left( B_1 + B_2 \left( \frac{T}{100} \right) + B_3 \left( \frac{T}{100} \right)^2 \right) \]

where:  
\[ T = \text{Absolute temperature (°K)} \]
\[ S = \text{Salinity} \]

<table>
<thead>
<tr>
<th>Gas</th>
<th>Source of experimental data</th>
<th>( A_1 )</th>
<th>( A_2 )</th>
<th>( A_3 )</th>
<th>( A_4 )</th>
<th>( B_1 )</th>
<th>( B_2 )</th>
<th>( B_3 )</th>
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</thead>
<tbody>
<tr>
<td>( \text{N}_2 )</td>
<td>Douglas (1964, 1965)</td>
<td>-173.2221</td>
<td>254.6078</td>
<td>146.3611</td>
<td>-22.0933</td>
<td>-0.054052</td>
<td>0.027266</td>
<td>-0.0038430</td>
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<tr>
<td></td>
<td>Murray et al. (1969)</td>
<td>(-172.4965)</td>
<td>(248.4262)</td>
<td>(143.0738)</td>
<td>(-21.7120)</td>
<td>(-0.049781)</td>
<td>(0.025018)</td>
<td>(-0.0034861)</td>
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<tr>
<td>( \text{O}_2 )</td>
<td>Carpenter (1966)</td>
<td>-173.9894</td>
<td>255.5907</td>
<td>146.4813</td>
<td>-22.2040</td>
<td>-0.037362</td>
<td>0.016504</td>
<td>-0.0020564</td>
</tr>
<tr>
<td></td>
<td>Murray and Riley (1969)</td>
<td>(-173.4292)</td>
<td>(249.6339)</td>
<td>(143.3483)</td>
<td>(-21.8492)</td>
<td>(-0.033096)</td>
<td>(0.014259)</td>
<td>(-0.0017000)</td>
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<tr>
<td>( \text{Ar} )</td>
<td>Douglas (1964, 1965)</td>
<td>-174.3732</td>
<td>251.8139</td>
<td>145.2337</td>
<td>-22.2046</td>
<td>-0.038729</td>
<td>0.017171</td>
<td>-0.0021281</td>
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<tr>
<td></td>
<td>Weiss (1971a)</td>
<td>(-173.5146)</td>
<td>(245.4510)</td>
<td>(141.8222)</td>
<td>(-21.8020)</td>
<td>(-0.034474)</td>
<td>(0.014934)</td>
<td>(0.0017729)</td>
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<tr>
<td>( \text{Ne} )</td>
<td>Weiss (1971b)</td>
<td>-166.8040</td>
<td>225.1946</td>
<td>140.8863</td>
<td>-22.6290</td>
<td>-0.127113</td>
<td>0.079277</td>
<td>-0.0129095</td>
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<td>(-160.2630)</td>
<td>(211.0969)</td>
<td>(132.1657)</td>
<td>(-21.3165)</td>
<td>(-0.122883)</td>
<td>(0.077055)</td>
<td>(-0.0125568)</td>
<td></td>
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<tr>
<td>( \text{He} )</td>
<td>Weiss (1971b)</td>
<td>-163.4207</td>
<td>216.3442</td>
<td>139.2032</td>
<td>-22.6202</td>
<td>-0.44781</td>
<td>0.023541</td>
<td>-0.0034266</td>
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<tr>
<td></td>
<td>(-152.9405)</td>
<td>(196.8840)</td>
<td>(126.8015)</td>
<td>(-20.6767)</td>
<td>(-0.040543)</td>
<td>(0.021315)</td>
<td>(0.0030732)</td>
<td></td>
</tr>
</tbody>
</table>
# Seawater Gas Concentrations in Equilibrium With the Atmosphere

## Table 6.2
NAECs of Gases in Seawater at a Salinity of 35.0.

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>30</th>
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</thead>
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</tr>
</tbody>
</table>

**Saturation Water Vapor Pressure** \( \left( \frac{P_{H_2O}}{P_T} \times 100 \right) \)

<table>
<thead>
<tr>
<th>Concentrations in mmol/m³</th>
<th>0.6%</th>
<th>0.8%</th>
<th>1.2%</th>
<th>1.6%</th>
<th>2.3%</th>
<th>3.1%</th>
<th>4.1%</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>635.7</td>
<td>565.6</td>
<td>508.3</td>
<td>460.7</td>
<td>420.4</td>
<td>385.7</td>
<td>355.1</td>
</tr>
<tr>
<td>O₂</td>
<td>355.6</td>
<td>313.2</td>
<td>278.7</td>
<td>250.0</td>
<td>225.9</td>
<td>205.1</td>
<td>186.9</td>
</tr>
<tr>
<td>CO₂</td>
<td>23.37</td>
<td>19.26</td>
<td>16.09</td>
<td>13.6</td>
<td>11.61</td>
<td>10.00</td>
<td>8.66</td>
</tr>
<tr>
<td>Ar</td>
<td>17.01</td>
<td>14.98</td>
<td>13.33</td>
<td>11.96</td>
<td>10.81</td>
<td>9.81</td>
<td>8.93</td>
</tr>
</tbody>
</table>

**Concentrations in μmol/m³**

<table>
<thead>
<tr>
<th>N₂O</th>
<th>14.84</th>
<th>12.16</th>
<th>10.09</th>
<th>8.46</th>
<th>7.16</th>
<th>6.10</th>
<th>5.23</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>8.45</td>
<td>8.03</td>
<td>7.66</td>
<td>7.33</td>
<td>7.04</td>
<td>6.79</td>
<td>6.56</td>
</tr>
<tr>
<td>Kr</td>
<td>4.31</td>
<td>3.68</td>
<td>3.18</td>
<td>2.78</td>
<td>2.44</td>
<td>2.16</td>
<td>1.93</td>
</tr>
<tr>
<td>CH₄</td>
<td>3.44</td>
<td>3.00</td>
<td>2.64</td>
<td>2.35</td>
<td>2.12</td>
<td>1.92</td>
<td>1.76</td>
</tr>
<tr>
<td>He</td>
<td>1.81</td>
<td>1.76</td>
<td>1.73</td>
<td>1.68</td>
<td>1.67</td>
<td>1.62</td>
<td>1.62</td>
</tr>
</tbody>
</table>

**NAEC** = normal atmospheric equilibrium concentration
8) \( % \text{ Saturation} _{G_{\text{sw}}} = \frac{P_{G(\text{seawater})}}{P_{G(\text{atmosphere})}} \cdot 100 \% = \frac{C_G}{NAEC} \cdot 100\% \)

Examples:

100% Saturation: Gas and liquid phases in equilibrium
\[
(P_{G(\text{seawater})} = P_{G(\text{atmosphere})})
\]

<100% Saturation: Gas transfer into solution (undersaturated)
\[
(P_{G(\text{seawater})} < P_{G(\text{atmosphere})})
\]

>100% Saturation: Gas transfer out of solution (supersaturated)
\[
(P_{G(\text{seawater})} > P_{G(\text{atmosphere})})
\]
Example: Calculation of % Saturation of Mediterranean Outflow Water

Loss of $O_2$ in Mediterranean bottom waters =

$$\text{NAEC}_{\text{Original watermass}} - [O_2]_{\text{Measured in outflow}}$$

From Table 6.2 or 8.3, T and S data
VALUES FOR THE IDEAL GAS CONSTANT "R" IN VARIOUS UNITS:

\[
\begin{align*}
8.3143 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} & \quad \text{(SI)} \\
82.058 \text{ cm}^3 \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\
0.082058 \text{ l} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\
1.9872 \times 10^{-3} \text{ Kcal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}
\end{align*}
\]

Conversion factors for pressure:

1 atm = 760 torr = 760 mm Hg
\[
\begin{align*}
= 1.013 \times 10^5 \text{ N} \cdot \text{m}^{-2} & = 1.013 \times 10^5 \text{ Pa} \\
= 1.013 \text{ bar} \\
= 14.70 \text{ lb} \cdot \text{in}^{-2} \\
= 1.013 \times 10^6 \text{ dyne cm}^{-2}
\end{align*}
\]

0.1 bar = 1 decibar

In seawater:

1 dbar \approx 1 \text{ m depth}

---

**Table 7.3. Factors for the interconversion of dissolved oxygen data**

\[
1 \text{ mmol } \text{O}_2 = 2 \text{ mg-at } \text{O} = 31.9988 \text{ mg } \text{O}_2 = 22.3916 \text{ ml } \text{O}_2 \text{ (STP)}
\]
Vertical Distribution of $O_2$

Dominant trends:

- Sub-thermocline $O_2$ minimum
- $O_2$ depletion at depth: Atlantic < Indian < Pacific
- High $O_2$ solubility in cold high-latitude water
- Low $O_2$ concs in upwelled waters
West-coast upwelling systems: Eastern Tropical North Pacific (ETNP)  Peru  Namibia

Figure 5.3.7: Oxygen concentration at the depth of the vertical oxygen minimum. Data are from the World Ocean Atlas 2001. [Conkright et al., 2002]
Eastern Tropical North Pacific (ETNP)
Hydrogen Sulfide – a gas under certain conditions

\[ S^{2-} + H^+ \leftrightarrow HS^- \]

\[ HS^- + H^+ \leftrightarrow H_2S \]

Under acidic conditions: neutral species that obeys gas laws

**Hydrogen sulphide**

As with dissolved oxygen the concentrations of hydrogen sulphide present in water samples may be expressed in a number of units depending on the purpose of the investigation. Hydrogen sulphide is usually produced in estuarine waters by bacterial reduction of sulphate and occurs in the water mainly as undissociated \( H_2S \) and \( HS^- \). At pH values below 11 only minute amounts of \( S^{2-} \) are present and \( H_2S \) dominates at pH values less than about 7 (Almgren et al., 1976). Thus the concentrations of the dissolved species are often expressed as in terms of the volume of the undissociated gas at STP per litre of solution, although mg \( S^{2-} \) l\(^{-1} \) is also used. As with oxygen and nutrient data, however, there is much to be gained from using molar units, in this case mmol \( S^{2-} \) l\(^{-1} \). Table 7.4 provides a summary of the relationships between the various units to be found in the literature.

**Table 7.4. Factors for the interconversion of dissolved hydrogen sulphide data**

<table>
<thead>
<tr>
<th>Molar Concentration</th>
<th>mg ( H_2S )</th>
<th>mg ( S^{2-} )</th>
<th>ml ( H_2S ) (STP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 mmol ( H_2S )</td>
<td>34.076</td>
<td>32.06</td>
<td>22.40</td>
</tr>
<tr>
<td>0.2935 mmol ( H_2S )</td>
<td>1 mg ( H_2S )</td>
<td>0.9408 mg ( S^{2-} )</td>
<td>0.657 ml ( H_2S ) (STP)</td>
</tr>
<tr>
<td>0.3119 mmol ( H_2S )</td>
<td>1.0629 mg ( H_2S )</td>
<td>1 mg ( S^{2-} )</td>
<td>0.699 mg ( H_2S ) (STP)</td>
</tr>
<tr>
<td>0.04464 mmol ( H_2S )</td>
<td>1.5213 mg ( H_2S )</td>
<td>1.4313 mg ( S^{2-} )</td>
<td>1 ml ( H_2S ) (STP)</td>
</tr>
</tbody>
</table>

(Head, 1985)
**Gas Hydrates (Clathrates)**

*Hydrate*: Crystalline structure of water in which hydrocarbon or CO$_2$ “gas” molecules are physically trapped (not bonded).

At appropriate T and P (above the freezing point of water) many gas hydrates are possible (up to iso-butane, C$_5$).

Of special interest: *Methane hydrate*
Methane Hydrate Stability-Field Diagram

Figure 1. Methane hydrate stability conditions for the pure methane-pure water and pure methane-seawater (S = 33.5 \%) systems over the pressure range of 2.56-12.0 MPa. Data for the pure methane-pure water system are from this study as well as those compiled in Sloan [1990]. Data for “synthetic” seawater (S = 35 \%) are from Dholabhai et al. [1991]. As shown in this figure, at any given pressure, the temperature at which methane hydrate dissociates in the pure methane-seawater system is depressed by approximately -1.1 °C relative to the pure methane-pure water system. Note the pressure axis is reversed in order to reflect increasing pressure with depth along continental margins, and that the temperature axis is expressed in °C (rather than K) for convenience. The depth axis assumes a hydrostatic pressure gradient of 0.010 MPa/m.
Seismic and Geochemical Evidence for Hydrates

Seismic profiles – **Bottom-simulating reflector (BSR)** seen cutting across bedding planes (at the base of the hydrate stability field).

**Sediment cores:**
- Will degas and “self-extrude” when brought to the ocean surface
- “Burning ice”
- Negative chloride anomalies

**Fig. 1.** (Left) Seismic reflection profile across the Blake Ridge showing locations of sites 994, 995, and 997 with respect to the bottom-simulating reflector. (Right) Interstitial water chloride values at these sites are shown.
Hydrate-Associated Chloride Anomalies

• During hydrate formation: water + methane are removed from pore water – leaves chloride-enriched pore water
• Over time, locally elevated chloride concentrations diffuse away
• During core recovery: hydrate decomposes, releasing methane and water – leaves chloride-depleted pore water
A Global Inventory of Methane Hydrate Occurrence

http://walrus.wr.usgs.gov/globalhydrate/
Largest reservoirs:

- East coast of North America
- Arctic Ocean
- East coast of Australia
Importance of Methane Hydrates

• Energy source: Blake Plateau (off SE U.S.) alone contains enough methane to meet US natural gas needs for 100 years

• Methane is a potent greenhouse gas

• Climatic change or tectonic events may lead to catastrophic methane release via positive feedback:
  
  Increased global temp causes hydrate decomposition
  
  Release of methane to atm increases global warming
1) Calculate the concentration of dissolved molecular nitrogen ($N_2$) in freshwater that is in equilibration with the atmosphere at 27°C, 1 atm pressure, 100% RH. Give your answer in µM, µmol/kg, mg/L, and mL/L(STP).

2) If the salinity of this water is increased to 36 g/kg, and the water is allowed to re-equilibrate with the same atmosphere, what is the resulting dissolved nitrogen concentration? Give your answer in µM.

3) If the atmospheric pressure is then increased to 2 atm (keeping everything else constant), what is the resulting dissolved nitrogen concentration? Give your answer in µM.

Be sure to show all calculations and explain where all data come from!