Dissolved Gases in Seawater

- Fundamentals
- Solubility Relationships
- Air-Sea Exchange
- Departures from Ideality
- O₂ Dynamics (Intro)
DISSOLVED GASES IN THE OCEANS

SOURCES

1. Atmosphere (Major Term)
   \((N_2, O_2, Ar, \text{etc.})\)

2. Volcanic Activity \((H_2S)\)

3. Marine Production & Consumption Process
   a) Biological Activity
      \((NO_3^- \rightarrow N_2O, \text{respiration})\)
   b) radioactive Decay
      \(^{226}\text{Ra} \rightarrow ^{222}\text{Rn}\)
BASIC CONCEPTS

I. Dalton’s Law

\[ P_T = \Sigma P_i \sim P_{N_2} + P_{O_2} + P_{Ar} + P_{H_2O} + P_{CO_2} \]

II. Ideal Gas Law

\[ P_i = n_iRT/V \quad \text{where} \quad R = 82.05 \text{ cm}^3 \text{ atm mol}^{-1} \text{deg}^{-1} \]

III. \[ P_i = X_i [P_T - P_{H_2O}], \quad P_{H_2O} = (h/100) P_{H_2O-Sat} \]

IV. Henry’s Law

\[ C_i = K_i [P_i] \quad \quad P_i \sim f_i \]

at equilibrium \[ P_i (\text{soln}) = P_i (\text{air}) \]

\[ K_i = f (T,S,P) \]
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FIGURE 6.5. The effect of temperature on the solubility of gases in seawater.
<table>
<thead>
<tr>
<th>Species</th>
<th>$K_e$, (mol/L atm)</th>
<th>$K_m$, (mol/L atm)</th>
<th>$\phi$, cm^3 mol^{-1}</th>
<th>$\mu$, cm^3 g^{-1}</th>
<th>$\alpha$, cm^3 mol^{-1}</th>
<th>$\rho$, g cm^{-3}</th>
<th>$\sigma$, g cm^{-3}</th>
<th>$\zeta$, g cm^{-3}</th>
<th>$\chi$, g cm^{-3}</th>
<th>$C_{gas}$, g cm^{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>1.6 x 10^{-6}</td>
<td>1.4 x 10^{-6}</td>
<td>5.2 x 10^{-2}</td>
<td>7.4 x 10^{-3}</td>
<td>3.0 x 10^{-2}</td>
<td>3.2 x 10^{-2}</td>
<td>1.0 x 10^{-1}</td>
<td>2.0 x 10^{-1}</td>
<td>7.0 x 10^{-2}</td>
<td>2.0 x 10^{-2}</td>
</tr>
<tr>
<td>N₂O</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>H₂</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Ar</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>O₂</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>N₂</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

and α (see text)
EFFECT OF TEMPERATURE ON SOLUBILITY OF GASES IN SEAWATER

<table>
<thead>
<tr>
<th>Gas</th>
<th>0°C</th>
<th>25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>1.8 nM</td>
<td>1.7 nM</td>
</tr>
<tr>
<td>Ne</td>
<td>7.9</td>
<td>6.6</td>
</tr>
<tr>
<td>Kr</td>
<td>4.0</td>
<td>2.3</td>
</tr>
<tr>
<td>Xe</td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td>N$_2$</td>
<td>616 µM</td>
<td>383 µM</td>
</tr>
<tr>
<td>O$_2$</td>
<td>349</td>
<td>206</td>
</tr>
<tr>
<td>Ar</td>
<td>17</td>
<td>10</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>14</td>
<td>6</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>20</td>
<td>9</td>
</tr>
</tbody>
</table>
EFFECT OF SALINITY ON SOLUBILITY OF GASES (0°C)

<table>
<thead>
<tr>
<th>Gas</th>
<th>Water</th>
<th>Seawater</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>2.2 nM</td>
<td>1.8 nM</td>
</tr>
<tr>
<td>Ne</td>
<td>10</td>
<td>7.9</td>
</tr>
<tr>
<td>Kr</td>
<td>5.8</td>
<td>4.0</td>
</tr>
<tr>
<td>Xe</td>
<td>0.9</td>
<td>0.2</td>
</tr>
<tr>
<td>N₂</td>
<td>823 µM</td>
<td>616 µM</td>
</tr>
<tr>
<td>O₂</td>
<td>456</td>
<td>349</td>
</tr>
<tr>
<td>Ar</td>
<td>22</td>
<td>17</td>
</tr>
<tr>
<td>CO₂</td>
<td>23</td>
<td>20</td>
</tr>
</tbody>
</table>
where $T_k = ln \left( \frac{T}{273.15} \right)$, and $T$ is temperature (°C).

The concentrations and fitting equations in the footnotes are for saturation values of O$_2$, N$_2$, and He in units of umol/kg saltwater, and the fugacity coefficients of CO$_2$ and H$_2$S have been calculated from the fugacity coefficients given in Table 3A-1.
Dissolved Gases in Seawater

- Fundamentals
- Solubility Relationships
- Air-Sea Exchange
- Departures from Ideality
- $O_2$ Dynamics (Intro)
Fick’s First Law

\[ \frac{dC_i}{dt} = A \ D_i \ (dC_i/dz) \]

Where:

- \( A = \text{area} \)
- \( C_i = \text{concentration species } i \)
- \( D_i = \text{diffusion coefficient} \)
- \( Z = \text{thickness of diffusion layer} \)
<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>642</td>
<td>1433</td>
<td>916</td>
<td>1394</td>
<td>163</td>
<td>60.9</td>
</tr>
<tr>
<td>823</td>
<td>1975</td>
<td>167</td>
<td>193</td>
<td>177</td>
<td>64.4</td>
</tr>
<tr>
<td>650</td>
<td>1516</td>
<td>942</td>
<td>1475</td>
<td>164</td>
<td>64.3</td>
</tr>
<tr>
<td>151</td>
<td>010</td>
<td>149</td>
<td>272</td>
<td>380</td>
<td>68.3</td>
</tr>
<tr>
<td>287</td>
<td>196</td>
<td>273</td>
<td>290</td>
<td>367</td>
<td>71.0</td>
</tr>
<tr>
<td>623</td>
<td>1433</td>
<td>385</td>
<td>1394</td>
<td>168</td>
<td>60.6</td>
</tr>
<tr>
<td>649</td>
<td>001</td>
<td>450</td>
<td>1070</td>
<td>232</td>
<td>148</td>
</tr>
<tr>
<td>467</td>
<td>1048</td>
<td>491</td>
<td>1019</td>
<td>242</td>
<td>64.4</td>
</tr>
<tr>
<td>415</td>
<td>86</td>
<td>391</td>
<td>252</td>
<td>63.9</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>5°C</th>
<th></th>
<th>20°C</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>S&lt;sup&gt;c&lt;/sup&gt;</td>
<td>(S = 35)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>D (× 10&lt;sup&gt;5&lt;/sup&gt;)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Molecular diffusion coefficients and kinematic viscosity create greater temperature dependence for Schmidt numbers than for the gas.

And the only factor causing a small dependence on Sc opposite trends with diffusion coefficients is the kinetic viscosity. The kinetic viscosity is greater in seawater than in freshwater, and we assume here that this is the molecular diffusion coefficient. The kinematic viscosity of water, from P. J. M. 4 (1992), is 1.0. Table 9.1. The kinematic viscosity of water, 1.0. The molecular diffusion coefficient in Chapter 9. Table 9.1. The kinematic viscosity of water, 1.0. The molecular diffusion coefficient in Chapter 9. Table 9.1. The kinematic viscosity of water, 1.0. The molecular diffusion coefficient in Chapter 9. Table 9.1. The kinematic viscosity of water, 1.0. The molecular diffusion coefficient in Chapter 9. Table 9.1.
Molecular boundary layers near the interface become important as eddy motions for transport. The scales are called the viscous (momentum), thermal (heat) and diffuse (mass) scales. There are three different distances from the wall where molecular motions heat and mass are characterized by molecular diffusion coefficients of different magnitude: (0.01 cm$^2$ s$^{-1}$ for momentum, 0.01 cm$^2$ s$^{-1}$ for heat and 10$^{-3}$ cm$^2$ s$^{-1}$ for mass). Because random molecular motions of momentum, greater velocity, which is indicated here by the length of the arrow in the eddy, because random molecular motions of momentum, the size of the water near the air-water interface decreases as the air-water interface is approached. The larger eddies have velocity of the water and the size of eddies in the water decrease as the air-water interface is approached. The larger eddies have a schematic representation of the boundary layers for momentum, heat and mass near the air-water interface.
Models for Air-Sea Gas Exchange

1) Stagnant Film (simplest)

2) Surface Renewal

3) Rigid Wall (Mathematically complex)
Figure 10.2. A schematic diagram of the stagnant molecular layers near the air–water interface. Fugacity in the bulk atmosphere and concentration in the water are indicated by $f^a$ and $[C]$, respectively. Chemical equilibrium at the air–water interface is described by Henry's Law, where $K_{HF_{sat}} = [C_{sat}]$. 
Combining Henry’s and Fick’s Laws:

\[ \frac{dC_i}{dt} = \left( \frac{A D_i H_i}{\delta} \right) [P_i \text{ (gas)} - (P_i \text{ (liquid)})] \]

where:

\[ \tau = \text{thickness of boundary layer} \]
More simply:

\[ F_i = \frac{dC_i}{dt} = G_c K_i \Delta P_i \]

\[ G_c = G* \left( \frac{D_i}{\nu} \right)^n = G* \left( Sc_i \right)^{-n} \]

Where:

- \( F \) = flux (mol cm\(^{-2}\) s\(^{-1}\))
- \( \Delta P_i \) = change in partial pressure across interface (mol cm\(^{-3}\))
- \( Sc_i \) = Schmidt number
- \( \nu \) = kinematic velocity
- \( G* \) = transfer velocity (cm s\(^{-1}\))
  = permeability coefficient
  = mass transfer coefficient
  = exit coefficient
  = piston velocity
FIGURE 6.2. The thickness of the laminar layer as a function of the wind speed.
Models for Air-Sea Gas Exchange

1) Stagnant Film

\[ G_c = \frac{D_i}{\delta} \]

2) Surface Renewal

\[ G_c = 2 \left( \frac{D_i}{\pi \theta} \right)^{0.5} \]

\( \theta \) is renewal time

3) Rigid Wall

\[ G_c = \frac{U^*}{12} \left( \frac{D_i}{\nu} \right)^{2/3} \]

\[ = \frac{U^*}{12} \left( Sc_i \right)^{-2/3} \]

\( U^* \) is the friction velocity at the interface
Wind speed at 10 m, $U_{10}$ (m s$^{-1}$)

$G_{600}$ = 0.23 $U_{10}$ + 0.1

through the dual tracer data

middle, which is the best fit

the addition of the one in the

in the caption to Figure 10.6. With

are the same as those described

and from the Florida Shell lines

experiments. N is from the George’s Bank

speed, $U_{10}$. For all dual tracer

velocity, $G_{600}$ as a function of wind

Figure 10.7: Gas Transfer
Dissolved Gases in Seawater

- Fundamentals
- Solubility Relationships
- Air-Sea Exchange
- Departures from Ideality
- O₂ Dynamics (Intro)
Figure 10.8. Measured oxygen concentrations in ocean surface waters as a function of temperature and salinity. The line marks the saturation value with atmospheric oxygen at a salinity of 35. Ocean data from the WOCE data base. WOCE bottle data.
Causes of Non-Reactive Gases Departing from Expected Solution:

1. Departures from Standard Atmosphere
2. Dissolution of Air Bubbles
3. Air Injection
4. Differential Heating and Gas Exchange
5. Mixing of Waters of Different Temperatures
6. Radiogenic or Primordial Addition
Figure 10.10: A schematic diagram illustrating two mechanisms of bubble-induced gas exchange at the air-water interface. Surrounding water before they exchange. They interact partly with the gas mixture by waves and exchange. $V_e$ is for larger bubbles that are indicated by the empirical constant wave exchange (partial trapping). $V_{w}$ is indicated by smaller bubbles that collapse totally as they are subducted into the water by a total exchange. Air injection (total exchange) Air injection (total exchange) Air injection (total exchange)
The intensity of acoustic backscatter is a function of depth in the ocean at 20 kHz. The intensity of acoustic backscatter is 12 m s⁻¹, backscattered intensity is an indication of the depth of breaking waves. (Data courtesy of Science, Sidney, B.C.).
Figure 10.11

A schematic diagram of steady-state gas supersaturation caused by bubble processes when there is no net flux at the air-water interface. The small symbols represent gas molecules in the air and dissolved in the water. The greater concentration of gas-water interface, FWI, indicated on the left side, induces flux, FB, into surface waters, illustrated on the right side of the diagram. This indicates that the dissolved gas is supersaturated in the water. The bubble-free surface water interface, FWI, = FB = GC.[CO] - [CSat].
BUBBLE INJECTION EFFECTS

1. Less soluble gases become more enriched in bubbles

2. Diffusion coefficients are approximately double in bubbles

3. Bubbles are pushed to depths of 20 m ($P_t \sim 3$ atm)

4. Air Injection- the total dissolution of the air in a bubble due to hydrostatic pressure

<table>
<thead>
<tr>
<th>Gas</th>
<th>$N_2$</th>
<th>$O_2$</th>
<th>Ar</th>
<th>$CO_2$</th>
<th>Ne</th>
<th>He</th>
<th>He</th>
<th>Kr</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta%$ sat</td>
<td>+7.7</td>
<td>+3.8</td>
<td>+3.5</td>
<td>+0.1</td>
<td>+11.6</td>
<td>+13.8</td>
<td>+1.8</td>
<td></td>
</tr>
</tbody>
</table>

From the total dissolution of a bubble (1 cm$^3$) of air at STP ($15^\circ$C and $S = 35$) in 1 m$^3$
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- $O_2$ Dynamics (Intro)
\[ \% \text{O}_2 \text{ sat} = \frac{\text{O}_2 \text{ obs}}{\text{O}_2 \text{ sat}} \times 100 \]
\[ \text{AOU} = \text{O}_2 \text{ sat} - \text{O}_2 \text{ obs} \]
FIGURE 6.9.
Profiles of oxygen in the North Atlantic and Pacific Oceans.
Figure 6.11. Profiles of temperature and oxygen in Pacific waters showing increases due to photosynthesis.
FIGURE 6.15. Differences in the measured and calculated dissolved oxygen concentrations in surface waters.
Figure 6.16: Apparent oxygen utilization in deep waters of the world oceans.
METHODS OF MEASUREMENT

1. Direct measurement in solution (O₂). Winkler Method for Oxygen

   A. MnSO₄ + NaOH Fixing Agent

      \[
      \text{Mn}^{2+} + 2 \text{OH}^- \rightarrow \text{Mn(OH)}_2
      \]
      \[
      2 \text{Mn(OH)}_2 + \text{O}_2 \rightarrow 2 \text{MnO(OH)}_2
      \]

   B. Add KI, HCl and titrate with S₂O₃²⁻

      \[
      \text{MnO(OH)}_2 + 4\text{H}^+ + 2 \text{I}^- \rightarrow \text{Mn}^{2+} + \text{I}_2 + 3\text{H}_2\text{O}
      \]
      \[
      \text{I}_3^- + 2 \text{S}_2\text{O}_3^{2-} \rightarrow 3 \text{I}^- + \text{S}_4\text{O}_6^{2-}
      \]

2. Gas Chromatography (O₂,N₂,Ar,CO,CH₄)

3. Mass Spectrometry (low or non-reactive gases)