There are several reasons for studying gas exchange. Three important ones are:

1. The ocean is a sink for anthropogenic CO$_2$ which is transferred to the ocean from the atmosphere by gas exchange.
2. Oxygen is a chemical tracer for photosynthesis. The gas exchange flux of O$_2$ is an important flux in box models of the euphotic zone for calculating net biological production.
3. Gas exchange is the process by which O$_2$ is transported into the ocean and is thus a control on aerobic respiration.

### I. Fundamental Properties of Gases

The relative composition of the main gases in the atmosphere (ratio of one gas to another) is nearly constant horizontally and vertically to almost 95 km. Atmospheric water (H$_2$O) is highly variable. Some trace gases involved in photochemical reactions can also be highly variable.

#### A. Composition of the Atmosphere

More than 95% of all gases except radon reside in the atmosphere. The atmosphere controls the oceans gas contents for all gases except radon, CO$_2$ and H$_2$O. Q. Can you explain why?

**Table 11-1**

<table>
<thead>
<tr>
<th>Gas</th>
<th>Mole Fraction in Dry Air ($f_G$)</th>
<th>Molar Volume at STP (l mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>0.78080</td>
<td>22.391</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0.20952</td>
<td>22.385</td>
</tr>
<tr>
<td>Ar</td>
<td>9.34 x 10$^{-3}$</td>
<td>22.386</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>3.3 x 10$^{-4}$</td>
<td>22.296</td>
</tr>
<tr>
<td>Ne</td>
<td>1.82 x 10$^{-5}$</td>
<td>22.421</td>
</tr>
<tr>
<td>He</td>
<td>5.24 x 10$^{-6}$</td>
<td>22.436</td>
</tr>
</tbody>
</table>

(See also Table 6.2 in Libes)

Some comments about units of gases:

**In Air**
- Pressure - Atmospheres
- 1 Atm = 760 mm Hg
- Partial Pressure of Gas$_i$ = P$_i$/760
- Volume - liters gas / liters air
- ppm = ml / l, etc

**In Water**
- Volume - liters gas at STP / kg$_{sw}$
- STP = standard temperature and pressure
- Molar - moles / kg$_{sw}$
- ppm = mg/l, etc
- Conversion: l$_{gas}$/kg$_{sw}$ = l$_{gas}$/mole = g/mole

($\approx$ 22.4 l/mol)

The pressure and volume units are the same at 760 mm Hg.
**Dalton's Law**

Gas concentrations are expressed in terms of pressures.

\[ \text{Total Pressure} = \Sigma P_i = \text{Dalton's Law of Partial Pressures} \]

\[ P_T = P_{N_2} + P_{O_2} + P_{H_2O} + \cdots \]

Dalton's Law implies ideal behavior -- i.e. all gases behave independently on one another (same idea as ideal liquid solutions with no electrostatic interactions). Gases are dilute enough that this is a good assumption.

Variations in partial pressure \( (P_i) \) result from:

1) variations in \( P_T \) (atmospheric pressure highs and lows)
2) variations in water vapor \( (P_{H_2O}) \)

We can express the partial pressure \( (P_i) \) of a specific gas on a dry air basis as follows:

\[ P_i = \left[ P_T - \frac{h}{100} P_o \right] f_i \]

where

- \( P_i \) = partial pressure of gas \( i \)
- \( P_T \) = Total atmospheric pressure
- \( h \) = % relative humidity
- \( P_o \) = vapor pressure of water at ambient \( T \)
- \( f_i \) = mole fraction of gas in dry air (see table above)

**Example:**

Say we have a humidity of 80% today and the temperature is 15°C

Vapor pressure of \( H_2O \) at 15°C = \( P_o = 12.75 \) (from reference books)

Then, \( P_{H_2O} = 0.80 \times 12.75 = 10.2 \) mm Hg

If \( P_T = 758.0 \) mm Hg

\( P_{TDry} = (758.0 - 10.2) \) mm Hg

\[ = 747.8 \text{ mm Hg} \]

Then: \( f_{H_2O} = \frac{P_{H_2O}}{P_T} = \frac{10.2}{758.0} = 0.013 \)

So for these conditions \( H_2O \) is 1.3% of the total gas in the atmosphere. That means that water has a higher concentration than Argon \((Ar)\). This is important because water is the most important greenhouse gas!
B. Solubility

The exchange or chemical equilibrium of a gas between gaseous and liquid phases can be written as:

\[ \text{A (g)} \rightleftharpoons \text{A (aq)} \]

At equilibrium we can define the familiar value

\[ K = \frac{[\text{A(aq)}]}{[\text{A(g)}]} \]

Q At equilibrium does gas A stop moving between gas and liquid phases?
No - only the net exchange is zero.

There are two main ways to express solubility.

1. Henry's Law:

   We can express the gas concentration in terms of partial pressure using the ideal gas law: \( PV = nRT \)
   so that the number of moles \( n \) divided by the volume is equal to \( [\text{A(g)}] \)
   \[ \frac{n}{V} = [\text{A(g)}] = \frac{P_A}{RT} \]
   where \( P_A \) is the partial pressure of A

   Then \( \quad K = \frac{[\text{A(aq)}]}{P_A/RT} \)
   or \( \quad [\text{A(aq)}] = (K/RT) \cdot P_A \)
   \[ [\text{A(aq)}] = K_H \cdot P_A \]
   units for \( K \) are \( \text{mol kg}^{-1} \text{ atm}^{-1} \); for \( P_A \) are atm in \( \text{mol kg}^{-1} \)

   Henry's Law states that the solubility of a gas is proportional its overlying partial pressure. The table given below (from Broecker and Peng, 1982, p. 112) summarizes values of Henry's Law constants for different gases.

Example (From Table 11-2):

The value of \( K_H \) for \( \text{CO}_2 \) at 24°C is \( 29 \times 10^{-3} \) moles kg\(^{-1}\) atm\(^{-1} \) or \( 2.9 \times 10^{-2} \) or \( 10^{-1.53} \).

The partial pressure of \( \text{CO}_2 \) in the atmosphere is increasing every day but if we assume that at some time in the recent past it was 350 ppm that is equal to \( 10^{-3.456} \) atm.

The concentration of \( \text{CO}_2 \) in water in equilibrium with that partial pressure is

\[ [\text{CO}_2(aq)] = K_H \cdot P_A \]
\[ = 10^{-1.53} \times 10^{-3.456} \]
\[ = 10^{-4.986} \text{ mol/l} \]

Example (Solubility at 0°C)(see also Table 11-3):

<table>
<thead>
<tr>
<th>Gas</th>
<th>( P_i )</th>
<th>( K_H ) (0°C, ( S = 35 ))</th>
<th>( C_i ) (0°C, ( S = 35; P = 760 \text{ mm Hg} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_2)</td>
<td>0.7808</td>
<td>0.80 x 10(^{-3})</td>
<td>62.4 x 10(^{-3}) mol kg(^{-1})</td>
</tr>
<tr>
<td>O(_2)</td>
<td>0.2095</td>
<td>1.69 x 10(^{-3})</td>
<td>35.4 x 10(^{-3})</td>
</tr>
<tr>
<td>Ar</td>
<td>0.0093</td>
<td>1.83 x 10(^{-3})</td>
<td>0.017 x 10(^{-3})</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>0.00033</td>
<td>63 x 10(^{-3})</td>
<td>0.021 x 10(^{-3})</td>
</tr>
</tbody>
</table>
### Table 11-2

Solubilities of various gases in sea water per atmosphere pressure of that gas.  

<table>
<thead>
<tr>
<th>Gas</th>
<th>Molecular Weight (g/mole)</th>
<th>Solubility Coefficient</th>
<th>Henry's Law Constant</th>
<th>Ratio of Solubility at 0°C to Solubility at 20°C</th>
<th>Volume Partition Coefficient (Air/Water) at 20°C</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>4</td>
<td>1.8</td>
<td>0.24</td>
<td>0.12</td>
<td>1.1</td>
<td>135</td>
</tr>
<tr>
<td>Ne</td>
<td>20</td>
<td>10.1</td>
<td>0.34</td>
<td>0.76</td>
<td>1.3</td>
<td>178</td>
</tr>
<tr>
<td>N₂</td>
<td>28</td>
<td>18.3</td>
<td>0.50</td>
<td>1.03</td>
<td>0.15</td>
<td>95</td>
</tr>
<tr>
<td>O₂</td>
<td>32</td>
<td>30.7</td>
<td>1.10</td>
<td>1.03</td>
<td>0.15</td>
<td>95</td>
</tr>
<tr>
<td>Ar</td>
<td>40</td>
<td>42.1</td>
<td>1.85</td>
<td>1.03</td>
<td>0.15</td>
<td>95</td>
</tr>
<tr>
<td>Kr</td>
<td>84</td>
<td>85.6</td>
<td>2.08</td>
<td>1.03</td>
<td>0.15</td>
<td>95</td>
</tr>
<tr>
<td>Xe</td>
<td>133</td>
<td>132</td>
<td>2.13</td>
<td>1.03</td>
<td>0.15</td>
<td>95</td>
</tr>
<tr>
<td>Rn</td>
<td>222</td>
<td>206</td>
<td>2.61</td>
<td>1.03</td>
<td>0.15</td>
<td>95</td>
</tr>
<tr>
<td>CO₂</td>
<td>44</td>
<td>1837</td>
<td>6.6</td>
<td>2.2</td>
<td>1.5</td>
<td>655</td>
</tr>
<tr>
<td>N₂O</td>
<td>44</td>
<td>1071</td>
<td>2.6</td>
<td>2.2</td>
<td>2.1</td>
<td>665</td>
</tr>
<tr>
<td>CO</td>
<td>137</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*The solubilities of He, Ne, O₂, N₂, Ar and CO₂ in sea water are those recommended by W. A. Sherwood in the Handbook of Chemistry and Physics with the salt effect extrapolated from other gases.

**Average density of sea water = 1.025 g/cm³**

(Personal communication P.W. Bulle and F.S. Liss, East Anglia Univ., Norwich, England)

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### Figure 11-1

**Figure 11-1**: The solubilities of various gases in sea water as a function of temperature. The units are standard cubic centimeters of gas contained by a liter of water per atmosphere of pressure exerted by the gas.
2. Bunson Coefficients

Since oceanographers frequently deal with gas concentrations not only in molar units but also in ml/l, we can also define

\[ [A(aq)] = \alpha P_A \]

where \( \alpha = 22,400 \times K_H \) (e.g., one mol of gas occupies 22,400 cm\(^3\) at STP)

\( \alpha \) is called the Bunsen solubility coefficient. Its units are cm\(^3\) mol\(^{-1}\). Appropriate values are summarized in the table below from Broecker and Peng (1982, p. 111)

**Summary of trends in solubility:**

1. Type of gas: \( K_H \) goes up as molecular weight goes up (note that CO\(_2\) is anomalous)
   
   Q. Why?

2. Temperature: solubility goes up as Temperature goes down
   
   Q. Can you explain why?

3. Salinity: solubility goes up as S goes down
   
   Q. Can you explain why?

Causes of deviations from Equilibrium:

Refer back to the graph of oxygen versus Temperature in ocean surface water (Lecture 9). Causes of deviation from saturation can be caused by:

1. nonconservative behavior (e.g. photosynthesis (+) or respiration (-) or denitrification (+))
2. bubble or air injection (+)
3. subsurface mixing - possible supersaturation due to non linearity of \( K_H \) or \( \alpha \) vs. T.
4. change in atmospheric pressure - if this happens quickly, surface waters cannot respond quickly enough to reequilibrate.

Table 11-3

<table>
<thead>
<tr>
<th>Gas</th>
<th>Partial Pressure in Dry Air atm</th>
<th>24°C Equilibrium Concentration in Surface Sea Water</th>
<th>29°C Equilibrium Concentration in Surface Sea Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>( 5.2 \times 10^{-6} ) atm</td>
<td>( 4.1 \times 10^{-5} ) cc/liter</td>
<td>( 1.8 \times 10^{-9} ) moles/kg</td>
</tr>
<tr>
<td>Ne</td>
<td>( 1.8 \times 10^{-5} ) atm</td>
<td>( 1.8 \times 10^{-5} ) cc/liter</td>
<td>( 7.9 \times 10^{-9} ) moles/kg</td>
</tr>
<tr>
<td>N(_2)</td>
<td>0.781</td>
<td>14.3</td>
<td>6.2 \times 10^{-4}</td>
</tr>
<tr>
<td>O(_2)</td>
<td>0.209</td>
<td>8.1</td>
<td>3.5 \times 10^{-4}</td>
</tr>
<tr>
<td>Ar</td>
<td>( 9.3 \times 10^{-6} ) atm</td>
<td>( 9.4 \times 10^{-5} ) cc/liter</td>
<td>( 4.2 \times 10^{-9} ) moles/kg</td>
</tr>
<tr>
<td>Kr</td>
<td>( 1.1 \times 10^{-6} ) atm</td>
<td>( 1.7 \times 10^{-5} ) cc/liter</td>
<td>( 7.2 \times 10^{-10} ) moles/kg</td>
</tr>
<tr>
<td>Xe</td>
<td>( 8.6 \times 10^{-6} ) atm</td>
<td>( 6.5 \times 10^{-6} ) cc/liter</td>
<td>( 3.7 \times 10^{-10} ) moles/kg</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>3.2 \times 10^{-4} atm</td>
<td>0.46</td>
<td>2.0 \times 10^{-5}</td>
</tr>
<tr>
<td>N(_2)O</td>
<td>3.0 \times 10^{-7} atm</td>
<td>2.1</td>
<td>1.4 \times 10^{-8}</td>
</tr>
</tbody>
</table>

*Salinity is assumed to be 35.000%/oo.*
II. Rates of Gas Exchange

There are many non-equilibrium situations for which we'd like to know the rate of gas exchange to estimate the time for gases to reach equilibrium.

The most common model is the thin film or Stagnant Boundary Layer Model.

The model is set up as shown schematically below. It assumes there is a well mixed atmosphere and a well mixed surface ocean where transport is controlled by turbulent diffusion separated by a stagnant film on the water side if the interface where transport is controlled by molecular diffusion. For more detail see Liss and Slater (1974) Nature, 247, 181-184.

Fig 11-2

The rate of transfer across this stagnant film occurs by molecular diffusion from the region of high concentration to the region of low concentration. Transport is described by Fick's First Law which states simply that flux is proportional to concentration gradient.

\[ F = -D \frac{\delta[A]}{\delta Z} \]

where

- \( D \) is the molecular diffusion coefficient which is a function of the specific gas and temperature.

- \( \delta[Z] \) is the thickness of the stagnant film (\( Z_{film} \))

- \( \delta[A] \) is the concentration difference across the film. The water at the top of the stagnant film is assumed to be in equilibrium with the atmosphere. We can calculate this value using the Henry's Law equation given above. The bottom of the film has the same concentration as the mixed-layer (\( C_l \)).

Thus: \[ F = - \frac{D}{Z_{film}} (C_g - C_l) = - \frac{D}{Z_{film}} (K_H P_g - C_l) \]
Because $D/Z_{\text{film}}$ has velocity units, it has been called the **Piston Velocity**
e.g., $D = \text{cm}^2 \text{ sec}^{-1}$
\[Z_{\text{film}} = \text{cm}\]

Typical values are $D = 1 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$
\[Z_{\text{film}} = 10 \text{ to } 60 \mu\text{m} \text{ (see Figure 11-3)}\]

Example:
$D = 3 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$
$Z_{\text{film}} = 17 \mu\text{m}$ determined for the average global ocean using $^{14}\text{C}$ data

Thus $Z_{\text{film}} = 1.7 \times 10^{-3} \text{ cm}$

The piston velocity is $D/Z = 1 \times 10^{-5}/1.7 \times 10^{-3}$
\[= 0.59 \times 10^{-2} \text{ cm/sec}\]
\[\approx 5 \text{ m/d}\]

Each day a 5 m thick layer of water will exchange its gas with the atmosphere. For a 100m thick mixed layer the exchange will be completed every 20 days.

The idea is that even when there is gaseous equilibrium, e.g. there is no gradient $(C_g - C_I)$, there is still exchange of gases at the rate of the piston velocity.
Think of two imaginary pistons: one moving upward through the water pushing ahead of it a column of gas with the concentration of gas in the upper ocean $(C_I)$ and one moving down into the sea carrying a column of gas with the concentration of gas in the top of the stagnant film $(C_g)$.
Even if the ocean and atmosphere are in gaseous equilibrium the transfer of gas continues but the amount "pushed in" just equals the amount "pushed out".

Q. Under what conditions would you expect maximum rates of gas exchange?
   a) thin film
   b) large conc. gradient
   c) high $D$ (high $T$ or low molecular weight gas)

Note: There are several other gas exchange models with increasing sophistication (e.g. the surface renewal model - Libes p. 97), but the stagnant film model is most widely known and utilized. This is the only gas exchange model you need to know for OCN 421.
Problems

1. Gas Exchange - O2

Calculate the residence time of O2 ocean mixed layer with respect to gas exchange. Assume the stagnant boundary layer model applies. Use the following values for possibly required parameters at 25°C.

\[ Z_{film} = 40 \, \mu m = 40 \times 10^{-6} m \]

\[ DO2 = 5 \times 10^{-2} m^2 y^{-1} \]

Mixed layer depth = 100m

\[ O_2 \text{ concentration in mixed layer} = 200 \, mmol \, m^{-3} = 200 \, \mu mol \, l^{-1} \]

\[ PO2, \, atm = 0.20 \, atm \]

\[ K_H \text{ for } O_2 = 1 \, mol \, m^{-3} \, atm^{-1} \]

Do the following:

a) Draw a picture of the gas exchange model
b) Calculate the piston velocity.
c) What is the \( O_2 \) (aq) at the top of the stagnant film?
d) What is the net gas exchange flux across the air-sea interface?
e) Calculate the "piston velocity" flux of \( O_2 \) across the atmosphere/ocean interface. (not the net gas exchange flux). This is the piston velocity times the \( O_2 \) at the top of the stagnant film layer.
f) Calculate the inventory of \( O_2 \) in the mixed layer. What are the units?
g) Calculate the residence time of \( O_2 \) in the mixed layer with respect to the "piston velocity" flux of \( O_2 \).


The average partial pressure of \( N_2O \) in the atmosphere over the Arabian Sea was 313 ppmv or \( 10^{-6.50} \) atm.

The Henry’s Law constant for \( N_2O \) solubility at 25\(^\circ\) C is \( K_H = 10^{-1.59} \) mol l\(^{-1}\) atm\(^{-1}\).

a. What was the mean saturated concentration of \( N_2O \) in surface water in mol l\(^{-1}\).
b. The average degree of supersaturation was 130% and the average piston velocity for the average wind speed was 22.7 cm hr\(^{-1}\). Calculate the average gas exchange flux using the stagnant boundary layer model. (10 points)

3. During our recent cruise to the Santa Barbara Basin the surface \( O_2 \) was 300 \( \mu mol \, kg^{-1} \) and it appeared to be at steady state. The water temperature was 25°C.

a) What was the magnitude of the gas exchange flux of \( O_2 \) and which direction did it go? Show all your work and explain your steps.

Important information:

assume 1 l = 1 kg

atmospheric \( P_{O2} = 0.20 \)

Henry's Law constant for \( O_2 \) in seawater at 25°C = \( 1.26 \times 10^{-3} \) mol l\(^{-1}\) atm\(^{-1}\)

molecular diffusion coefficient for \( O_2 \) at 25°C = \( 2.0 \times 10^{-5} \) cm\(^2\) sec\(^{-1}\)
the film thickness = 50 µm = 5 x 10^{-3} cm

b) One student exclaimed "Hey, we can calculate the biological productivity from this flux". What do you think he had in mind? Show how you can do this and calculate the productivity in the units mmol C m^{-2} d^{-1}. What assumptions do you have to make to do this calculation?

c) Is this productivity total, new or regenerated? Explain your answer.

4. Consider the reaction:
   \[ \text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \]

   a) Define and explain the difference between the thermodynamic equilibrium constant (K_2) and the apparent equilibrium constant (K_2'). What are the advantages and disadvantages of both when conducting equilibrium calculations.
   b) The best value for K_2 is 4.67 x 10^{-11} and for K_2' is 7.9 x 10^{-10}. Are these values consistent with the speciation of major ions in seawater as predicted by Garrels and Thompson? They calculated that the % free for CO_3^{2-} and HCO_3^- were 9% and 69% respectively. They used free ion activity coefficients of 0.20 and 0.68 respectively.
References:


