

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

1. The ocean is a sink for anthropogenic CO₂ 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 O₂ is an important flux in box models of the euphotic zone for calculating net biological production.
3. Gas exchange is the process by which O₂ 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 (H₂O) 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, CO₂ and H₂O.

Q. Can you explain why?

Table 11-1

| <u>Gas</u> | <u>Mole Fraction in Dry Air (f_G)</u> where f _G = moles gas i/total moles | <u>molar volume at STP (l mol⁻¹)</u> |
|-----------------|---|---|
| N ₂ | 0.78080 | 22.391 |
| O ₂ | 0.20952 | 22.385 |
| Ar | 9.34 x 10 ⁻³ | 22.386 |
| CO ₂ | 3.3 x 10 ⁻⁴ | 22.296 |
| Ne | 1.82 x 10 ⁻⁵ | 22.421 |
| He | 5.24 x 10 ⁻⁶ | 22.436 |

(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
= 1 atm. 0°C
Molar - moles / kg_{sw}
Conversion: l_{gas}/kg_{sw} / l_{gas} / mole = moles/kg_{sw}

(~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.

Total Pressure = ΣP_i = Dalton's Law of Partial Pressures

$$P_T = P_{N_2} + P_{O_2} + P_{H_2O} + \dots\dots\dots$$

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:

$$P_i = [P_T - h/100 P_O] f_i$$

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

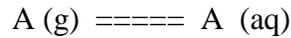
$$\begin{aligned} P_{TDry} &= (758.0 - 10.2) \text{ mm Hg} \\ &= 747.8 \text{ mm Hg} \end{aligned}$$

Then: $f_{H_2O} = P_{H_2O} / P_T = 10.2 / 758.0 = 0.013$

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:



At equilibrium we can define the familiar value

$$K = [A(aq)] / [A(g)]$$

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 $[A(g)]$

$$n/V = [A(g)] = P_A / RT \quad \text{where } P_A \text{ is the partial pressure of } A$$

Then $K = [A(aq)] / P_A/RT$

or $[A(aq)] = (K/RT) P_A$

$$[A(aq)] = K_H P_A \quad \text{units for } K \text{ are } \text{mol kg}^{-1} \text{ atm}^{-1}; \text{ for } P_A \text{ are atm}$$

in 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 CO_2 at 24°C is $29 \times 10^{-3} \text{ moles kg}^{-1} \text{ atm}^{-1}$ or 2.9×10^{-2} or $10^{-1.53}$.

The partial pressure of 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 $10^{-3.456} \text{ atm}$.

The concentration of CO_2 in water in equilibrium with that partial pressure is

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

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

| Gas | P_i (from page 1) | $K_H(0^\circ\text{C}, S = 35)$ (from Table 11-2) | $C_i(0^\circ\text{C}, S = 35; P = 760 \text{ mm Hg})$ |
|---------------|------------------------|---|---|
| N_2 | 0.7808 | 0.80×10^{-3} | $62.4 \times 10^{-3} \text{ mol kg}^{-1}$ |
| O_2 | 0.2095 | 1.69×10^{-3} | 35.4×10^{-3} |
| Ar | 0.0093 | 1.83×10^{-3} | 0.017×10^{-3} |
| CO_2 | 0.00033 | 63×10^{-3} | 0.021×10^{-3} |

Table 11-2

FROM BROECKER AND PENC (1982)

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

| Gas | Molecular Weight g/mole | BUNSON COEFFICIENT Solubility cc/liter | | HENRY'S LAW CONSTANT Solubility** 10 ⁻³ moles/kg | | Ratio of Solubility at 0°C to Solubility at 24°C | Volume Partition Coefficient (Air/Water) at 24°C | Ref. |
|--------------------|-------------------------|--|------|---|------|--|--|-------|
| | | 0°C | 24°C | 0°C | 24°C | | | |
| He | 4 | 7.8 | 7.4 | 0.34 | 0.32 | 1.1 | 135 | (655) |
| Ne | 20 | 10.1 | 8.6 | 0.44 | 0.37 | 1.2 | 116 | (655) |
| N ₂ | 28 | 18.3 | 11.8 | 0.80 | 0.51 | 1.6 | 85 | (653) |
| O ₂ | 32 | 38.7 | 23.7 | 1.69 | 1.03 | 1.6 | 42 | (653) |
| Ar | 40 | 42.1 | 26.0 | 1.83 | 1.13 | 1.6 | 39 | (654) |
| Kr | 84 | 85.6 | 46.2 | 3.8 | 2.1 | 1.8 | 22 | (658) |
| Xe | 131 | 192 | 99 | 8.4 | 4.3 | 1.9 | 10 | (660) |
| Rn | 222 | 406 | 186 | 17.8 | 8.1 | 2.2 | 5.4 | (660) |
| CO ₂ | 44 | 1437 | 666 | 63 | 29 | 2.2 | 1.5 | (656) |
| N ₂ O | 44 | 1071 | 476 | 47 | 21 | 2.2 | 2.1 | (659) |
| CCl ₃ F | 137 | - | 677 | - | 29 | - | 1.5 | (+) |

*The solubilities of He, Ne, O₂, N₂, Ar and CO₂ in sea water are those recommended by Weiss of Scripps Institution of Oceanography. The solubilities of Xe and Rn are from the CRC 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. Balls and P.S. Liss, East Anglia Univ., Norwich, England.

SOLUBILITY INCREASES WITH MOLE WT AND DECREASING TEMP.

i.s. $K_H = 2.9 \times 10^{-3} \text{ mol/ks}^{-1}$
 $= 2.9 \times 10^{-2}$
 $= 10^{-1.53}$

CONCENTRATION RATIO FOR EQUAL VOLUME OF AIR AND SEAWATER

Figure 11-1

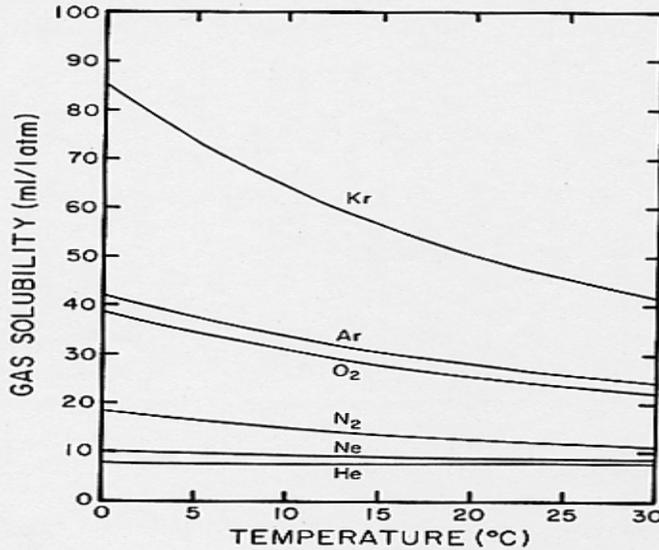


Figure 1. The solubilities of various gases in sea water as a function of temperature. The units are standard cubic centimeters of gas contained by a liter of water per atmosphere of pressure exerted by the gas.

2. Bunsen 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 cm³ at STP)
 α is called the Bunsen solubility coefficient. Its units are cm³ 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 CO₂ 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 α vs. T.
4. change in atmospheric pressure - if this happens quickly, surface waters cannot respond quickly enough to reequilibrate.

Table 11-3

Table 11-3 Equilibrium concentrations of various gases in surface ocean water.*

| Gas | Partial Pressure in Dry Air atm | Equilibrium Concentration in Surface Sea Water | | | |
|------------------|---------------------------------|--|----------------------|-----------------------|-----------------------|
| | | cc/liter | | moles/kg | |
| | | 0°C | 24°C | 0°C | 24°C |
| He | 5.2×10^{-6} | 4.1×10^{-5} | 3.8×10^{-5} | 1.8×10^{-9} | 1.7×10^{-9} |
| Ne | 1.8×10^{-5} | 1.8×10^{-4} | 1.5×10^{-4} | 7.9×10^{-9} | 6.7×10^{-9} |
| N ₂ | 0.781 | 14.3 | 9.2 | 6.2×10^{-4} | 4.0×10^{-4} |
| O ₂ | 0.209 | 8.1 | 5.0 | 3.5×10^{-4} | 2.2×10^{-4} |
| Ar | 9.3×10^{-3} | 0.39 | 0.24 | 1.7×10^{-5} | 1.1×10^{-5} |
| Kr | 1.1×10^{-6} | 9.4×10^{-5} | 5.1×10^{-5} | 4.2×10^{-9} | 2.3×10^{-9} |
| Xe | 8.6×10^{-8} | 1.7×10^{-5} | 8.5×10^{-6} | 7.2×10^{-10} | 3.7×10^{-10} |
| CO ₂ | 3.2×10^{-4} | 0.46 | 0.21 | 2.0×10^{-5} | 9.3×10^{-6} |
| N ₂ O | 3.0×10^{-7} | 3.2×10^{-4} | 1.4×10^{-4} | 1.4×10^{-6} | 6.3×10^{-6} |

*Salinity is assumed to be 35.00‰.

II. Rates of Gas Exchange

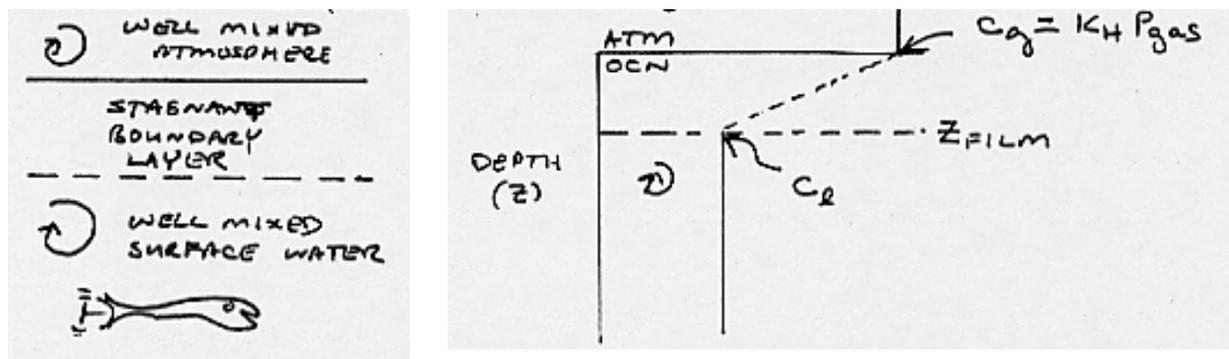
There are many non-equilibrium situations for which we'd like to know the rate of gas exchange to estimate the time for gases to reach equilibrium.

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 of 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..

$$F = -D \delta[A] / \delta Z$$

where

D is the molecular diffusion coefficient which is a function of the specific gas and temperature.

δZ 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).

$$\text{Thus: } F = -D/Z_{\text{film}} (C_g - C_l) = -D/Z_{\text{film}} (K_H P_g - C_l)$$

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

Example:

$$D = 3 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$$

$Z_{\text{film}} = 17 \text{ } \mu\text{m}$ determined for the average global ocean using ^{14}C data

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

$$\begin{aligned} \text{The piston velocity} &= D/Z = 1 \times 10^{-5} / 1.7 \times 10^{-3} \\ &= 0.59 \times 10^{-2} \text{ cm/sec} \\ &\approx 5 \text{ m / d} \end{aligned}$$

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 ($C_g - C_l$), 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_l) 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).

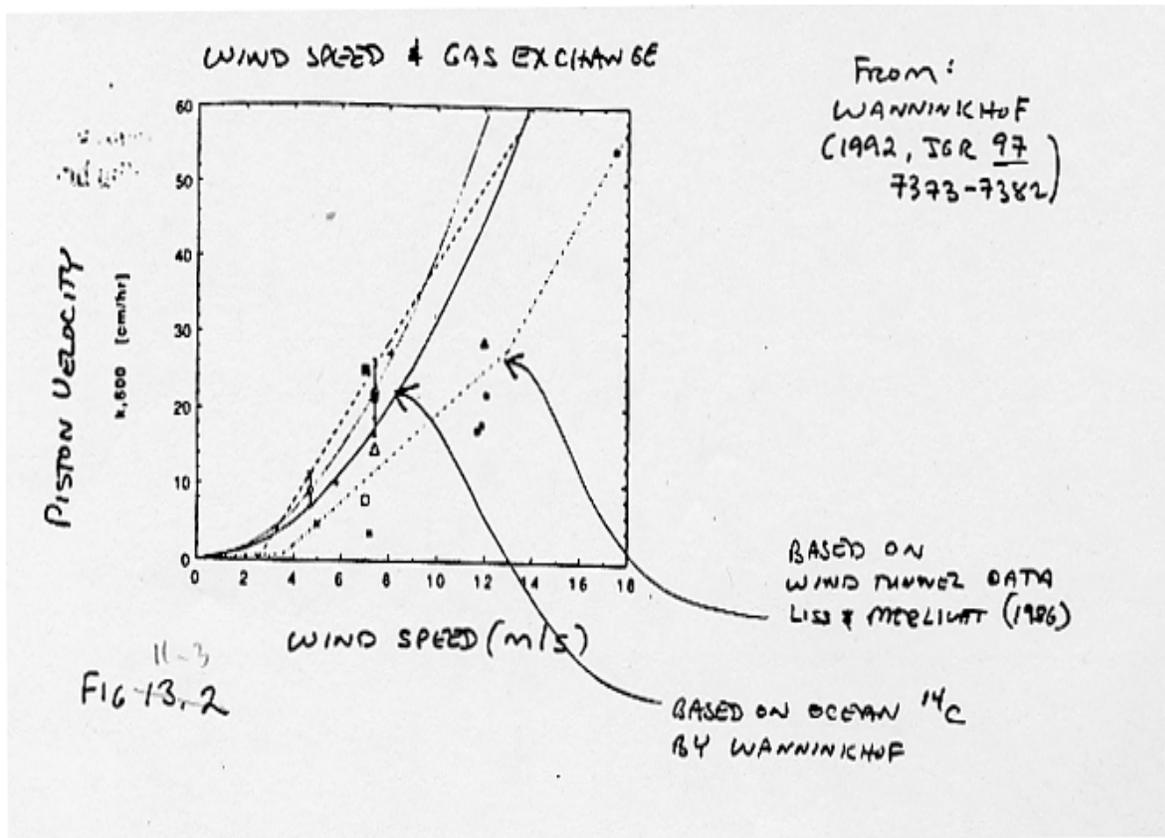
Even if the ocean and atmosphere are in gaseous equilibrium the transfer of gas continues but the amount "pushed in" just equals the amount "pushed out".

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.

Fig 11-3



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.

$$Z_{\text{film}} = 40 \mu\text{m} = 40 \times 10^{-6}\text{m}$$

$$D_{\text{O}_2} = 5 \times 10^{-2} \text{ m}^2 \text{ y}^{-1}$$

Mixed layer depth = 100m

$$\text{O}_2 \text{ concentration in mixed layer} = 200 \text{ mmol m}^{-3} = 200 \mu\text{mol l}^{-1}$$

$$P_{\text{O}_2, \text{atm}} = 0.20 \text{ atm}$$

$$K_{\text{H}} \text{ for O}_2 = 1 \text{ mol m}^{-3} \text{ atm}^{-1}$$

Do the following:

- Draw a picture of the gas exchange model
- Calculate the piston velocity.
- What is the O₂ (aq) at the top of the stagnant film?
- What is the net gas exchange flux across the air-sea interface?
- Calculate the "piston velocity" flux of O₂ across the atmosphere/ocean interface. (not the net gas exchange flux). This is the piston velocity times the O₂ at the top of the stagnant film layer.
- Calculate the inventory of O₂ in the mixed layer. What are the units?
- Calculate the residence time of O₂ in the mixed layer with respect to the "piston velocity" flux of O₂.

2. A recent paper reported data for the gas nitrous oxide (N₂O) in the surface waters of the Arabian Sea (Lal and Patra, 1998, Global Biogeochemical Cycles, 12, 321-327).

The average partial pressure of N₂O in the atmosphere over the Arabian Sea was 313 ppmv or $10^{-6.50}$ atm.

The Henry's Law constant for N₂O solubility at 25° C is $K_{\text{H}} = 10^{-1.59} \text{ mol l}^{-1} \text{ atm}^{-1}$.

- What was the mean saturated concentration of N₂O in surface water in mol l⁻¹.
- 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 O₂ was 300 μmol kg⁻¹ and it appeared to be at steady state. The water temperature was 25°C.

- What was the magnitude of the gas exchange flux of O₂ 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 O₂ in seawater at 25°C = $1.26 \times 10^{-3} \text{ mol l}^{-1} \text{ atm}^{-1}$

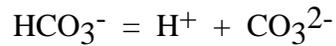
molecular diffusion coefficient for O₂ at 25°C = $2.0 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$

the film thickness = $50 \mu\text{m} = 5 \times 10^{-3} \text{ cm}$

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 $\text{mmol C m}^{-2}\text{d}^{-1}$. 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:



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 4.67×10^{-11} and for K_2' is 7.9×10^{-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:

Broecker W.S. and T.-H. Peng (1974) Gas Exchange rates between air and sea. *Tellus*, 26, 21-35.

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Wanninkhof R. (1992) Relationship between wind speed and gas exchange over the sea. *J. Geophys. Res.*, 97, 7373-7382.

Watson A.J., R.C. Upstill-Goddard and P.S. Liss (1991) Air-Sea gas exchange in rough and stormy seas measured by a dual-tracer technique. *Nature*, 349, 145-147.