Dissolved Gases other than Carbon Dioxide in Seawater

OCN 623 – Chemical Oceanography

16 February 2017

Reading: Libes, Chapter 6 – pp. 147-158 and 164-168

Student Learning Outcomes (SLOs)

At the completion of this section, students should be able to:

1. Explain the concept of gas partial pressure, and calculate partial pressure from mole fraction and total pressure data

2. Use the Ideal Gas Law to convert between molar and volume units for gas concentrations

3. Use Henry's Law to explain the equilibrium of gases between the ocean and the atmosphere

4. Use Weiss' equation to calculate the equilibrium of gases between the ocean and the atmosphere

5. Calculate the loss of dissolved oxygen in a water mass after it leaves the ocean surface.

Outline

1. Fundamental gas laws
2. Gas solubility
3. Normal atmospheric equilibrium concentration (NAEC)
4. Oceanic applications

Fundamental Gas Laws

1) In water: [G] = gas concentration of gas "G" in a solution (μmol/L, mL/L)

2) In gas mixture: $P_{Total} = P_{N_2} + P_{O_2} + P_{Ar} + P_{H_2O} + \ldots$ (Dalton's Law)

P_G = partial pressure (atm or kPa) of gas "G"

3) In gas mixture: $P_G = P_{Total} \cdot$ (mole fraction of "G" in a gas mixture)

> In the atmosphere (at 1atm TOTAL pressure and 100% relative humidity):
>
> $P_{N_2} = 0.78$ atm $\quad P_{CO_2} = 0.00038$ atm
>
> $P_{O_2} = 0.21$ atm $\quad P_{CH_4} = 0.0000014$ atm

Poll

The mole fraction of Argon (Ar) in air is 0.009 (0.9%).

What is its partial pressure in air at sea level?

1) 0.9 atm
2) 0.09 atm
3) 0.009 atm ←
4) 0.0009 atm

What is its partial pressure in air that is compressed to 10 atm?

1) 0.9 atm
2) 0.09 atm ←
3) 0.009 atm
4) 0.0009 atm

4) IDEAL GAS LAW: $P_{Total}V = nRT$ (for a closed system)

(V = volume, n = # of moles, R = ideal gas constant, T = ºK)

> AT STP (0ºC *or* 273°K, 1atm) in the gaseous state:
>
> 1 mole = 22.4 L

5) HENRY'S LAW: $P_G = K_G \cdot [G]$ (under equilibrium conditions)

K_G = "Henry's Law Constant" (a function of S and T)

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

VALUES FOR THE IDEAL GAS CONSTANT "R" IN VARIOUS UNITS:

$8.3143\ J \cdot K^{-1} \cdot mol^{-1}$ (SI)

$82.058\ cm^3 \cdot atm \cdot K^{-1} \cdot mol^{-1}$

$0.082058\ l \cdot atm \cdot K^{-1} \cdot mol^{-1}$

$1.9872 \times 10^{-3}\ Kcal \cdot K^{-1} \cdot mol^{-1}$

Conversion factors for pressure:

1 atm = 760 torr = 760 mm Hg
= $1.013 \times 10^5\ N \cdot m^{-2}$ = 1.013×10^5 Pa
= 1.013 bar
= $14.70\ lb\ in^{-2}$
= $1.013 \times 10^6\ dyne\ cm^{-2}$

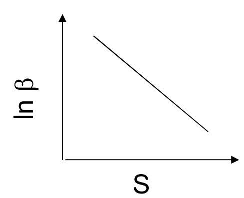
0.1 bar = 1 decibar

In seawater:
1 dbar ≈ 1 m depth

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

1 mmol O_2 = 2 mg-at O = 31.9988 mg O_2 = 22.3916 ml O_2 (STP)

6) Setchenow Relationship ("Salting-out Effect") for air-equilibrated water:



$\ln \beta = b_1 + (b_2 \cdot S)$

where b_1 and b_2 are constants for each gas for a given temp

Lower salinity -- higher solubility

7) Effect Of Salinity and Temperature on air-equilibrated water:

$$\ln [G] = A_1 + A_2(100/T) + A_3 \ln(T/100) + A_4 (T/100) + S [B_1 + B_2 (T/100) + B_3 (T/100)^2]$$

T = ºK S = salinity (Weiss, 1970)

Lower temp -- higher solubility

Constants are quoted for a given P_{Tot} (*e.g.*, Table 8.3) →

Gas Solubility - Empirical Data

$$\ln[G] = A_1 + A_2(100/T) + A_3 \ln(T/100) + A_4(T/100) + S\left(B_1 + B_2(T/100) + B_3(T/100)^2\right)$$

where: T = Absolute temperature (°K), S = Salinity (g/kg)

TABLE 8.3

***Solubility of gases** in sea water with the constants for equation (8.11) to yield c_G^* in μmol kg^{-1} (values in parentheses yield cm^3 l^{-1}) relative to air at 760 mm Hg total pressure at 100% relative humidity.*

Gas	Source of experimental data	A_1	A_2	A_3	A_4	B_1	B_2	B_3
N_2	Douglas (1964, 1965)	−173·2221	254·6078	146·3611	−22·0933	−0·054052	0·027266	−0·0038430
	Murray *et al.* (1969)	(−172·4965)	(248·4262)	(143·0738)	(−21·7120)	(−0·049781)	(0·025018)	(−0·0034861)
O_2	Carpenter (1966)	−173·9894	255·5907	146·4813	−22·2040	−0·037362	0·016504	−0·0020564
	Murray and Riley (1969)	(−173·4292)	(249·6339)	(143·3483)	(−21·8492)	(−0·033096)	(0·014259)	(−0·0017000)
Ar	Douglas (1964, 1965)	−174·3732	251·8139	145·2337	−22·2046	−0·038729	0·017171	−0·0021281
	Weiss (1971a)	(−173·5146)	(245·4510)	(141·8222)	(−21·8020)	(−0·034474)	(0·014934)	(0·0017729)
Ne	Weiss (1971b)	−166·8040	225·1946	140·8863	−22·6290	−0·127113	0·079277	−0·0129095
		(−160·2630)	(211·0969)	(132·1657)	(−21·3165)	(−0·122883)	(0·077055)	(−0·0125568)
He	Weiss (1971b)	−163·4207	216·3442	139·2032	−22·6202	−0·44781	0·023541	−0·0034266
		(−152·9405)	(196·8840)	(126·8015)	(−20·6767)	(−0·040543)	(0·021315)	(0·0030732)

Seawater Gas Concentrations in Equilibrium With the Atmosphere

NAEC = Normal Atmospheric Equilibrium Concentration

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

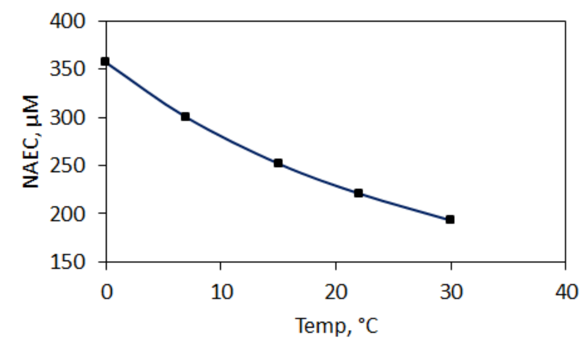
T(°C)	0	5	10	15	20	25	30
Saturation Water Vapor Pressure $\left(\frac{P_{H_2O}}{P_T} \times 100\right)$							
	0.6%	0.8%	1.2%	1.6%	2.3%	3.1%	4.1%
Concentrations in mmol/m^3							
N_2	635.7	565.6	508.3	460.7	420.4	385.7	355.1
O_2	355.6	313.2	278.7	250.0	225.9	205.1	186.9
CO_2	23.37	19.26	16.09	13.6	11.61	10.00	8.66
Ar	17.01	14.96	13.33	11.96	10.61	9.61	8.93
Concentrations in μmol/m^3							
N_2O	14.84	12.16	10.09	8.46	7.16	6.10	5.23
Ne	8.45	8.03	7.66	7.33	7.04	6.79	6.56
Kr	4.31	3.68	3.16	2.78	2.44	2.16	1.93
CH_4	3.44	3.00	2.64	2.35	2.12	1.92	1.76
He	1.81	1.76	1.73	1.68	1.67	1.62	1.62

How does the solubility of O_2 change with temperature?

Salinity = 35 g/kg

Temperature range: 0 – 30°C

Temp, °C	*NAEC, μM*
0	359
7	302
15	254
22	222
30	194



The Best Way to Obtain NAEC: Create a Spreadsheet

$$\ln[G] = A_1 + A_2(100/T) + A_3 \ln(T/100) + A_4(T/100) + S\left(B_1 + B_2(T/100) + B_3(T/100)^2\right)$$

Oxygen data (Weiss, 1970):								
A1 =	-173.4292		B1 =	-0.033096	Temp (C) =	15.0	Temp (K) =	288.15
A2 =	249.6339		B2 =	0.014259	Sal (g/kg) =	35.0		
A3 =	143.3483		B3 =	-0.001700				
A4 =	-21.8492							
ln $[O_2]$ =	1.7384							
$[O_2]$ =	5.6882	mL O_2 / L H_2O	← "Bunsen coefficient"					
	253.94	**μM (solution conc. in equil. w/ moist air @ 1 atm and given temp)**						

This spreadsheet uses data in Weiss (1970) for calculating O_2 in units of mL/L, and converts the result to μmol/L (μM)

You should create a similar spreadsheet for the homework assignment

The final “Gas Law”.....Percent Gas Saturation:

8) $\% \text{ Saturation}_{G_{sw}} = \frac{P_{G(seawater)}}{P_{G(atmosphere)}} \cdot 100\,\% \quad = \quad \frac{[G]}{NAEC} \cdot 100\%$

HENRY’S LAW: $P_{G\,(seawater)} = K_G \cdot [G]$

(under equilibrium conditions)

How to compare gas concentrations in atmosphere & seawater using the same measure

Examples:

100% Saturation: Gas and liquid phases in equilibrium

$(P_{G(seawater)} = P_{G(atmosphere)})$

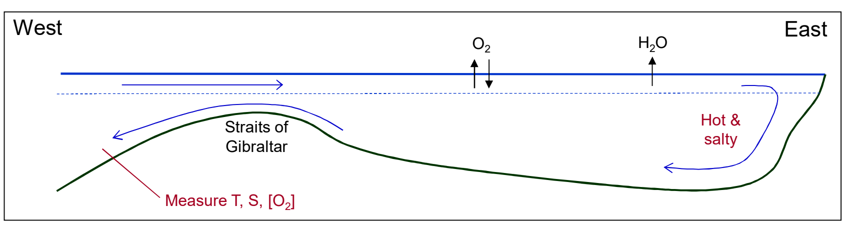
<100% Saturation: Gas transfer into solution (undersaturated)

$(P_{G(seawater)} < P_{G(atmosphere)})$

>100% Saturation: Gas transfer out of solution (supersaturated)

$(P_{G(seawater)} > P_{G(atmosphere)})$

Example: O_2 Deficit in Mediterranean Outflow Water



Loss of O_2 in Mediterranean bottom waters =

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

Computed from T and S data (or use Table 8.3 or 6.2)

Note: [O_2] is commonly known as “dissolved oxygen” or “DO”

Group Task

What is the loss of DO in Mediterranean bottom water if the outflow water has the following characteristics?

Salinity = 36.9 g/kg

Temperature = 19.0°C

$[O_2]$ = 210 μM

NAEC = 232 μM

Thus, loss of DO = 232 – 210 = 22 μM

Group Task

What is the loss of DO in Mediterranean bottom water in units of mL/L?

22 μM = 22 μmol/L_{sw} = ? mL/L_{sw}

PV = nRT   V = nRT/P

n = 22 μmoles   R = 0.082058 L atm K^{-1} mol^{-1}

T = 19.0°C = 19.0 + 273 = 292K

P = 1 atm

V = (22 umol) (10^{-6} mol/μmol) (0.082058 L atm/K/mol) (1000 mL/L) (309.9K) / 1 atm

V = 0.53 mL

$[O_2]$ = 0.56 mL/L_{sw}

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

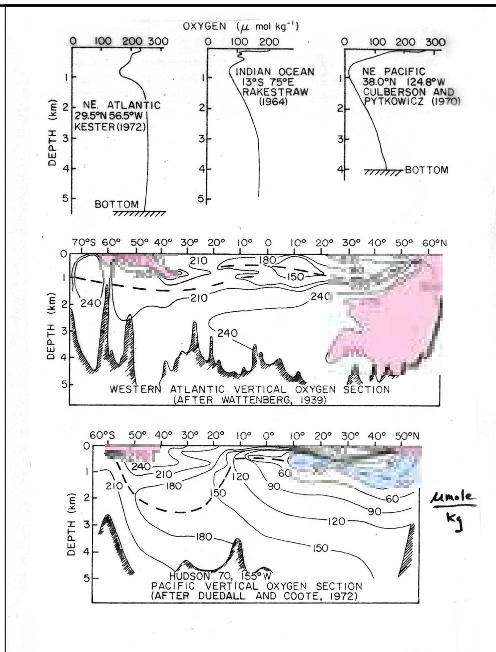


FIG. 8.7. Vertical distribution of oxygen in the ocean. Upper: profiles from three ocean basins; Centre: north–south vertical section through the western Atlantic; Lower: north–south vertical section through the central Pacific. The dashed line represents the depth of the oxygen minimum surface.

Horizontal Distribution of O_2

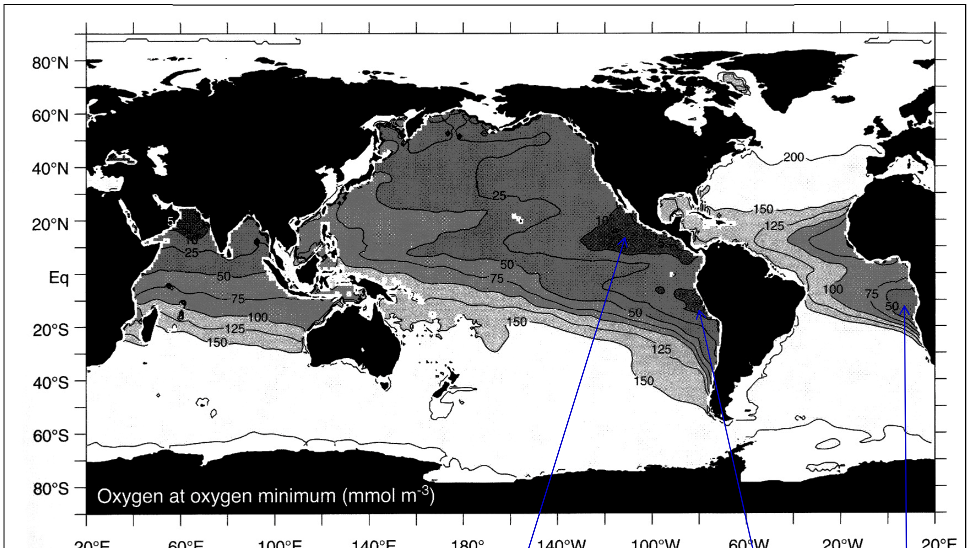
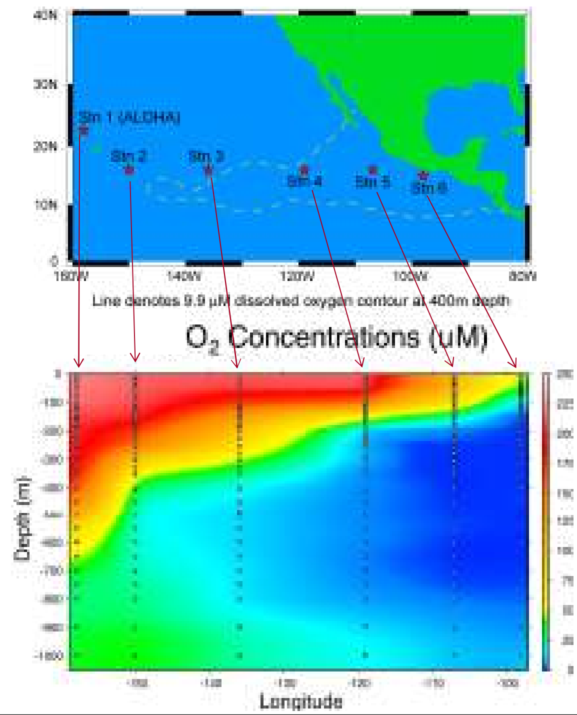


FIGURE 5.3.7: Oxygen concentration at the depth of the vertical oxygen minimum. Data are from the World Ocean Atlas 2001. [Conkright et al., 2002]

West-coast upwelling systems: Eastern Tropical North Pacific (ETNP) Peru Namibia

Eastern Tropical North Pacific (ETNP)



Sansone *et al.* 2001

Homework due: Tuesday, Feb 21, 2017

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, 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 decreased to 0.5 atm (keeping everything else constant), what is the resulting dissolved nitrogen concentration after re-equilibration? Give your answer in μM.

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

Carbon Dioxide, Alkalinity and pH

OCN 623 – Chemical Oceanography

21 February 2017

Reading: Libes, Chapter 15, pp. 383 – 389 (top of page)

(Remainder of chapter will be used with the classes “Global Carbon Dioxide” and “Biogenic production, carbonate saturation and sediment distributions”)