# Dissolved Gases other than Carbon Dioxide in Seawater

OCN 623 – Chemical Oceanography

*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 1atm TOTAL pressure and 100% relative humidity):

$P_{N_2} = 0.78\ \text{atm}$ $P_{CO_2} = 0.00032\ \text{atm}$

$P_{O_2} = 0.21\ \text{atm}$ $P_{CH_4} = 0.0000014\ \text{atm}$

4) IDEAL GAS LAW: $P_{Total}V = nRT$

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

AT STP (0ºC, 1atm) in the gaseous state:

1 mole = 22.4 L

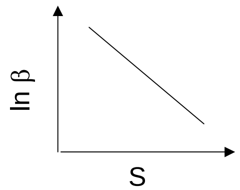
5) HENRY'S LAW: $P_G = K_G \cdot C_G$ (under equilibrium conditions)

$K_G$ = "Henry's Law Constant" (a function of salinity)

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

$$\left(\text{Units}: \frac{mL_{GAS}}{mL_{S.W.} \cdot atm}\right)$$

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 -- higher solubility

7) Effect Of Salinity And Temperature:

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

Lower temp -- higher solubility

T = °K S = salinity (Weiss, 1970)

Constants are quoted for a given $P_G$ (*e.g.*, Table 8.3)

# Gas Solubility - Empirical Data

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

where: T = Absolute temperature (°K)

S = Salinity

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

## Seawater Gas Concentrations in Equilibrium With the Atmosphere

**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/m³** | | | | | | |
| $N_2$ | 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 | 14.98 | 13.33 | 11.96 | 10.81 | 9.81 | 8.93 |
| | **Concentrations in µmol/m³** | | | | | | |
| $N_2O$ | 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 | 3.18 | 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 |

NAEC = normal atmospheric equilibrium concentration

8) % Saturation $_{G_{sw}} = \dfrac{P_{G(seawater)}}{P_{G(atmosphere)}} \cdot 100\,\% \quad = \quad \dfrac{C_G}{NAEC} \cdot 100\,\%$

Examples:

100% Saturation: Gas and liquid phases in equilibrium

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

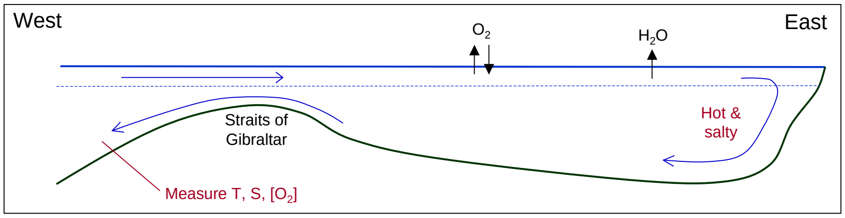
<100% Saturation: Gas transfer into solution (undersaturated)

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

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

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

# Example: Calculation of % Saturation of Mediterranean Outflow Water




Loss of $O_2$ in Mediterranean bottom waters =

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

From Table 6.2 or 8.3, T and S data

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

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

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

0.1 bar = 1 decibar

In seawater:

1 dbar ≈ 1 m depth

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

$1\ mmol\ O_2 = 2\ mg\text{-}at\ O = 31.9988\ mg\ O_2 = 22.3916\ ml\ O_2\ (STP)$

# Vertical Distribution of $O_2$

Dominant effects:

- 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

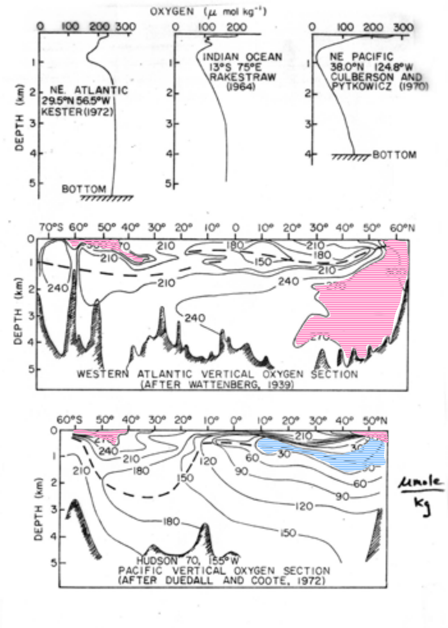



FIG. 8.7. Vertical distribution of oxygen in the ocean. Upper: profiles from three ocean basins; Centre: north–south vertical section through the western Atlantic; Lower: north–south vertical section through the central Pacific. The dashed line represents the depth of the oxygen minimum surface.

# Horizontal Distribution of $O_2$

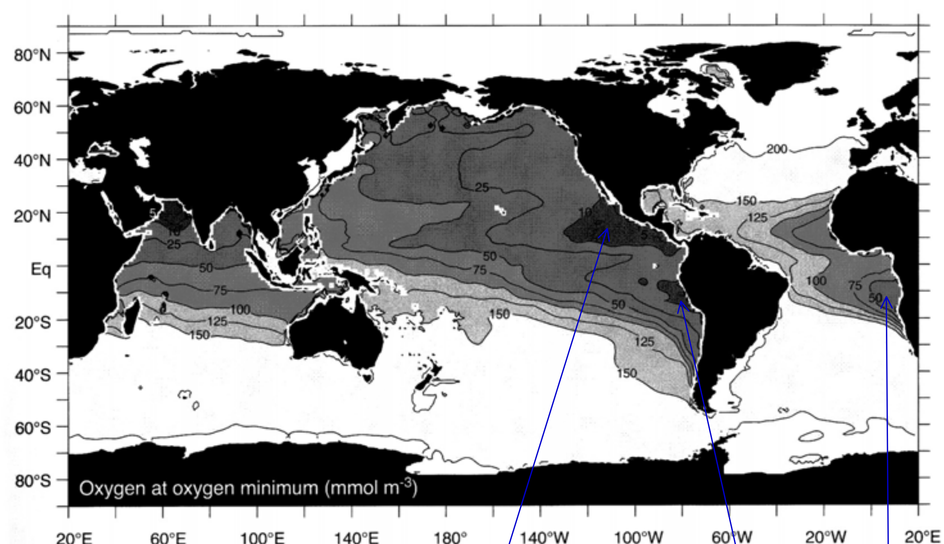
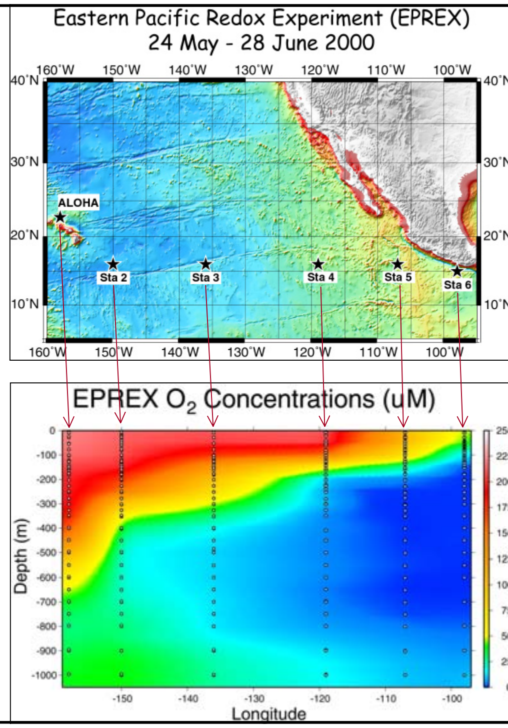



FIGURE 5.3.7: Oxygen concentration at the depth of the vertical oxygen minimum. Data are from the World Ocean Atlas 2001. [*Conkright et al.*, 2002]

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




# Hydrogen Sulfide – a gas under certain conditions

$$S^{2-} + H^{+} \leftrightarrow HS^{-}$$

$$HS^{-} + H^{+} \leftrightarrow H_2S$$

Ion

Dissolved gas

Under acidic conditions: neutral species that obeys gas laws

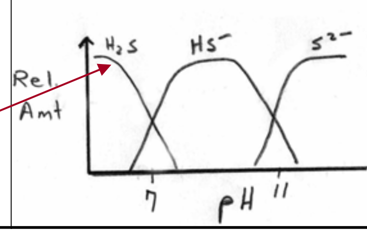
*Hydrogen sulphide*

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*

| |
|---|
| 1 mmol $H_2S$ = 34.076 mg $H_2S$ = 32.06 mg $S^{2-}$ = 22.40 ml $H_2S$ (STP) |
| 0.2935 mmol $H_2S$ = 1 mg $H_2S$ = 0.9408 mg $S^{2-}$ = 0.657 ml $H_2S$ (STP) |
| 0.3119 mmol $H_2S$ = 1.0629 mg $H_2S$ = 1 mg $S^{2-}$ = 0.699 mg $H_2S$ (STP) |
| 0.04464 mmol $H_2S$ = 1.5213 mg $H_2S$ = 1.4313 mg $S^{2-}$ = 1 ml $H_2S$ (STP) |

(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*

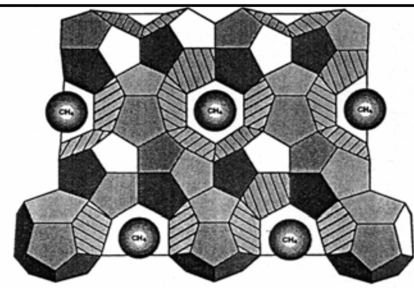


**Figure 1.** Gas hydrate structure. In this structure I methane hydrate the rigid cages are composed of hydrogen-bonded water molecules, and each cage, both exposed and covered in this figure, contains a methane molecule. Modified from *Hitchon* [1974].

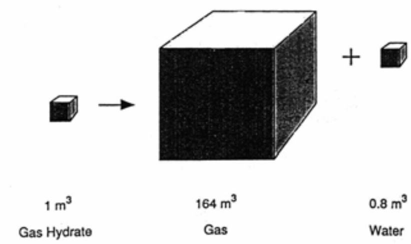



**Figure 2.** One cubic meter of gas hydrate yields 164 m$^3$ of gas and 0.8 m$^3$ of water at standard temperature and pressure.

# Methane Hydrate Stability-Field Diagram

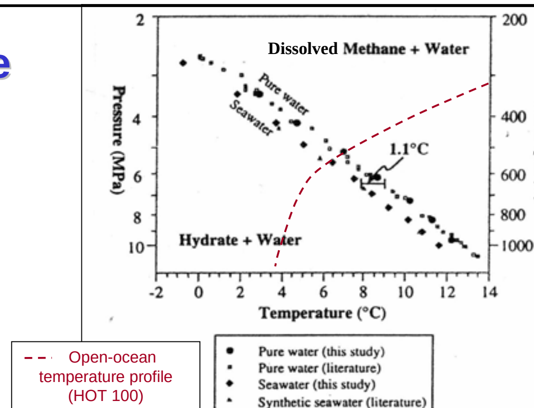



**Figure 1.** Methane hydrate stability conditions for the pure methane-pure water and pure methane-seawater (S ≈ 33.5 ‰) systems over the pressure range of 2.56-12.0 MPa. Data for the pure methane-pure water system are from this study as well as those compiled in *Sloan* [1990]. Data for "synthetic" 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

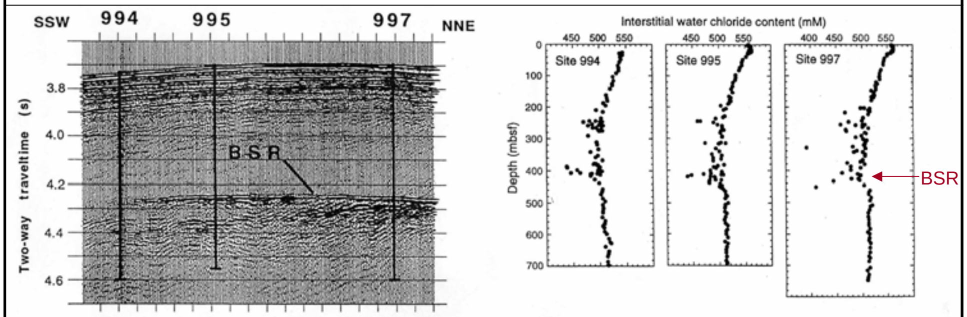



*Fig. 1. (Left) Seismic reflection profile across the Blake Ridge showing locations of sites 994, 995, and 997 with respect to the bottom-simulating reflector. (Right) Interstitial water chloride values at these sites are shown.*

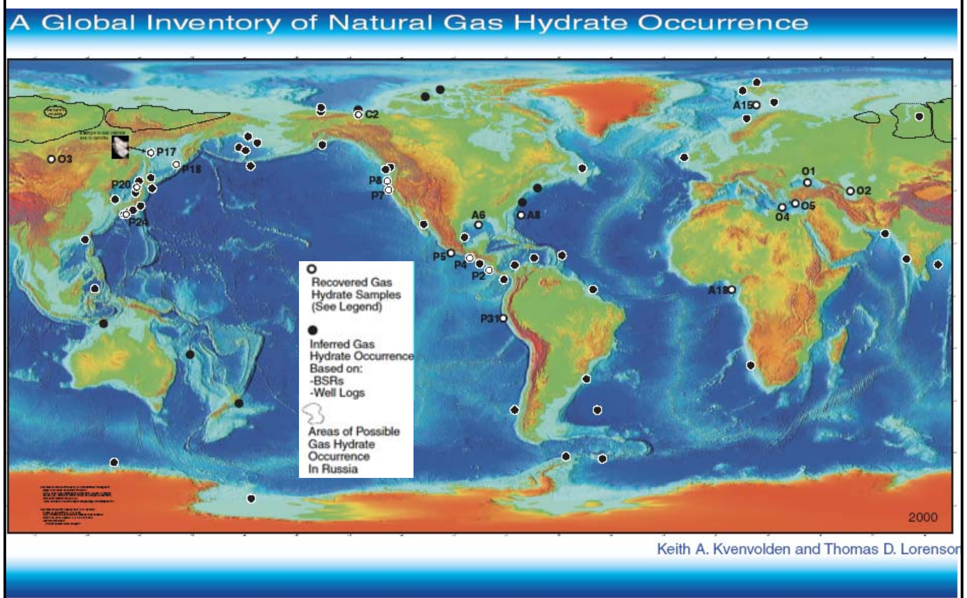
Seismic profiles – *Bottom-simulating reflector (BSR)* seen cutting across bedding planes (at the base of the hydrate stability field).

*Sediment cores:*

- Will degas and "self-extrude" when brought to the ocean surface
- "Burning ice"
- Negative chloride anomalies →

## 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




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

## 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

## OLD Homework due: Thursday, Feb 21, 2008

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, 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!

## OLD Homework due: Tuesday, Feb 6, 2007

1) Calculate (as opposed to look up in a table) the concentration of nitrogen in surface seawater (S = 35, T = 25°C) when in equilibrium with the atmosphere. Express your results in units of moles/L, moles/kg, and liters(STP)/L. Show your calculations!!

2) The solubility of methane in 25°C seawater with a salinity of 40 is 1.34 mmol/kg. The solubility in 25°C water with a salinity of 0 is 1.58 mmol/kg. Calculate the solubility of methane in 25°C seawater with a salinity of:

   a) 15

   b) 30