MARINE AND OCEAN CHEMISTRY

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Read the details of the information provided below from the sources recommended as a reference.

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3. Salinity, chlorinity, conductivity, and density
4. Major constituents of seawater
5. Simple gases
6. Salts in solution
7. Carbon dioxide
8. Nutrients
9. Trace metals and other minor elements
10. Chemical extraction of useful substances from the sea

References:

1. An Introduction to the Chemistry of the Sea, Michael E. Q. Pilson
2. Marine Chemistry & Geochemistry, John H. Steele et al.
3. Chemistry in the Marine Environment, R. E. Hester and R. M. Harrison
4. Marine Chemistry, P. J. Wangersky

SIMPLE GASES

1. Simple gas laws

2. Solubility in water

3. Sources and sinks within the ocean

4. Atmospheric exchange by diffusion

Concentrations of conservative gases in dry air, the solubility of each pure gas in pure water				
Gas	Symbol	Mole fraction in air	Solubility, μmol kg^{-1} bar^{-1}	Concentration mol kg^{-1}
Nitrogen	N_2	0.7808	695.0	537.4×10^{-6}
Oxygen	O_2	0.2095	1372.2	284.7×10^{-6}
Argon	Ar	0.00934	1508	13.95×10^{-6}
Neon	Ne	18.2×10^{-6}	462.0	8.328×10^{-6}
Helium	He	5.25×10^{-6}	385.4	2.00×10^{-6}
Krypton	Kr	1.14×10^{-6}	2764	3.12×10^{-6}
Xenon	Xe	0.087×10^{-6}	4996	0.434×10^{-6}

- The recommended SI unit of pressure is the Pascal, which is one Newton per square meter.

- The use of the bar (= 10^5 Pa) is in common use, and has the advantage that 1 bar is close to the standard atmospheric pressure.

SIMPLE GAS LAWS

For air:

$$p_T = pp(N_2) + pp(O_{2)}) + pp(Ar) + pp(H_2O) + \ldots$$

p_T = The total pressure

pp = The partial pressure

- Ideal gas law:

$$p\,V = n\,R\,T$$

- At STP (standard temperature and pressure: 0 °C or 273.15 K, and 1atmosphere pressure = 101 325 Pa) 1 mole of an ideal gas occupies a volume of 22.413 L.

- All real gases deviate slightly from the "ideal" behavior.

- For precise work, it is sometimes necessary to account for these deviations by using one of several possible equations of state with additional empirically measured terms, such as the so-called "virial equation":

$$P\,V_m = R\,T\left(1 + \frac{B_T}{V_m} + \dots\right)$$

V_m = The molar volume

B_T = The second of several virial coefficients (a function of temperature and is different for each gas)

- For accurate calculation of the situations that might be found under high pressures in the ocean, the virial equation or some other formulation is necessary.

SOLUBILITY IN WATER

- The amount of a gas dissolved in a quantity of water, when the gas and water phases are in equilibrium, is directly proportional to the pressure of the gas.

- Henry's law:

$$[G] = H_G \times pp(G)$$

[G] = The concentration of gas G in solution

pp(G) = The partial pressure of gas G

H_G = The Henry's law constant for gas G (a function of T and S)

- Since the major conservative gases in the atmosphere are present in very nearly constant proportions, it has been the usual oceanographic practice not to calculate from the Henry's law constant for each gas, or to give solubilities as concentrations in equilibrium with the pure gas.

- Instead, their solubilities are provided by tabulating their concentrations in seawater in equilibrium with the atmosphere, at 1 atmosphere total pressure, under specified conditions of temperature and salinity.

Concentrations of three major atmospheric gases in water and seawater

Gas	Air, %	Pure Water		Seawater, S = 35‰	
		0 °C	30 °C	0 °C	30 °C
		Concentrations (μmol kg^{-1})			
N_2	-	830.5	457.9	622.0	362.5
O_2	-	457.0	237.3	347.9	190.7
Ar	-	22.30	11.65	17.02	9.38
		Composition of total gas (mol%)			
N_2	78.08	63.4	64.8	63.02	64.4
O_2	20.95	34.9	33.6	35.3	33.9
Ar	0.934	1.70	1.65	1.72	1.67

SOURCES AND SINKS WITHIN THE OCEAN

- In addition to gain or loss by exchange with the atmosphere, there are two possibilities.

    1. Gases may be produced or consumed in situ.
    2. They may exchange with the sediments.

ATMOSPHERIC EXCHANGE BY DIFFUSION

- Both the air and the water are always in motion to some extent. Turbulent eddies commonly must keep both air and water mixed and chemically homogeneous at some distance above and below the interface.

- However, such eddies cannot penetrate exactly to the surface, and indeed, at some distance, perhaps very close to the interface, eddy motions must nearly vanish.

- A common way to imagine the situation is to consider that right at the interface there are **unstirred laminar boundary layers** that do not readily mix with the air above or the water below.

- For non-reactive gases, such as O_2, N_2, and the noble gases, it can be shown that they diffuse rapidly enough through the unstirred laminar boundary layer in the air that this is not a significant barrier. However, there is certainly a barrier imposed by the layer of unstirred water.

- For very reactive gases, such as SO_2 or NH_3, the reaction rate at the water surface is so great that diffusion in the boundary layer of the air limits transport rates so in such a situation this must also be considered.