Lecture 4 questions – Major Ions, Conservative Elements and Dissolved Gases

(1) True or false

(a) Conservative elements are not essential for life
(b) Only the major elements in seawater are conservative
(c) All major elements in seawater are conservative
(d) The concentration of conservative elements does not change in the oceans
(e) Non of the above

Gases

Gas	Mole Fraction in Dry Air (f_G)	Henry's Law Constant (mol/kg at 35‰; 760 mm Hg) K_H (10^{-3}) 0°C/24°C
Nitrogen (N_2)	78.084%	0.80/0.51
Oxygen (O_2)	20.952%	1.69/1.03
Argon (Ar)	0.934%	1.83/1.13
Carbon dioxide (CO_2	350ppm	63/29
Neon (Ne)	18ppm	0.44/0.37
Helium (He)	5ppm	0.34/0.32
Krypton (Kr)	1ppm	3.8/2.1
Xenon (Xe)	0.08ppm	8.4/4.3

$$[A(aq)] = K_H P_A$$

(2) Calculate concentration in solution of N_2, O_2, Ar, and CO_2, at 0°C and salinity of 35. From the Henry's Law coefficients where would you expect do most of these gases reside (in the ocean or the atmosphere)? Can you explain why?

N_2	624
O_2	354
Ar	17
CO_2	22

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_2O.

What is the ratio of nitrogen to oxygen in the atmosphere and in seawater? Which of the gases is more soluble?

At 0 degrees $P_{N2} = 0.781$, $P_{O2} = 0.209$
At equilibrium (saturation) $[N_2] = 624$ µmol/kg; $[O_2] = 354$µmol/kg
$P_{N2}/P_{O2}= 0.781/0.209= 3.7$ (about 4 times more N_2)
$[N_2]/[O_2]= 624/354 =1.76$ (only less than 2 times) e.g. oxygen more soluble

(3) Kr is an inert, non-reactive gas with an abundance of 1 ppm in the atmosphere (P_{Kr} = 10^{-6} atm). As the scientific advisor to Superman (who is about to dive to the bottom of the ocean to save a whale), you need to estimate the surface and deep-water concentrations of this deadly element. Based on your knowledge of ocean circulation and gas solubility, will the [Kr(aq)] increase or decrease with depth? Why? What will happen if this water will up well fast?

Kr is higher at depth because the temperature is lower.
2.1 nmol/kg at surface and 3.5 nmol/kg at depth; if the water were to up well fast the it would become supersaturated by 60%

(4) Explain why O_2 is supersaturated in surface waters. How can you calculate only the effect of photosynthesis? Would you expect the depth profile of oxygen to follow that of Kr?

Oxygen is supersaturated in the surface because of bubbles injection and input due to photosynthesis. To calculate the effect of photosynthesis we need to normalize to Ar or another refractory gas. The depth profiles of Kr and oxygen will be different since oxygen is consumed at depth by respiration.

(5) Mediterranean waters are warm (~25ºC) and salty. They have a higher density than the Atlantic surface waters. What is the oxygen concentration in the Mediterranean waters? As these waters sinks to ~1500m in the Atlantic they mix with colder waters and their temperature drops to 10 degrees. Will these waters be under-saturated or supersaturated? By how much?

$K_H = 1.34 \times 10^{-3}$ mol kg^{-1} atm^{-1} at 10°C;
$= 1.03 \times 10^{-3}$ mol kg^{-1} atm^{-1} at 25°C

First calculate the oxygen concentration at 25°C this is the concentration that will sink to 1500 m. At 10°C the saturation concentration would be higher therefore, the sample will be under saturated. 215-280 = 65; 65/280 = 23%

(6) Under what conditions would you expect maximum rates of gas exchange?

a) With a thin film layer (high wind).
b) With a large concentration gradient.
c) When a high diffusion rate (high T or low molecular weight gases)

(7) Gas Exchange - O_2

The flux, F, of oxygen across the air-water interface is proportional to the degree of saturation on average it is 3% supersaturated (e.g 103% saturation):

$$F_{O2} = G_{O2}\,\{[O_2] - [O_2]_S\} \;=\; -D/Z\ \ \{[O_2] - [O_2]_S\}$$

where: $[O_2]_S$ is the saturation value (moles/m^3)

G is an empirically determined mass transfer coefficient (piston velocity m/d) = -D/Z

Z film = 40 µm = 40×10^{-6} m $\qquad D_{O2} = 5 \times 10^{-2}\ m^2\ y^{-1}$

The mean saturation value in the surface ocean is 220×10^{-6} moles/l.

(a) Calculate the flux; would it be in or out of the ocean?

$G = -D/Z = 5 \times 10^{-2}\ m^2\ y^{-1}/40 \times 10^{-6}\ m = 1250\ m\ yr^{-1}$

$F_{O2} = (1250\ m/yr)\ [0.03\ (220 \times 10^{-3})\ mol/m^3] = 8.25\ mol\ O_2\ m^{-2}\ yr^{-1}$

The direction is out of the ocean.

Independent estimates of net biological oxygen production are more like *3-6* $mol\ O_2\ m^{-2}\ yr^{-1}$, the difference is most likely due to bubble addition.

(b) Calculate the residence time of O_2 in the ocean mixed layer with respect to gas exchange.

Mixed layer depth = 100m

Remember: This piston velocity flux is the piston velocity times the O_2 at the top of the stagnant film layer

What is the $O_2(aq)$ at the top of the stagnant film? 220 µmol

What is the net gas exchange flux across the air-sea interface? 1250m/yr or 3.4 m/day

Calculate the "piston velocity" flux of O_2 across the atmosphere/ocean interface.

$220\ mmol\ m^{-3} \times 3.4\ m\ day^{-1} = 748\ mmol\ m^{-2}\ day^{-1}$

Calculate the inventory of O_2 in the mixed layer. What are the units? ($220\ mmol\ m^{-3}$ X $100m = 22\ moles\ m^{-2}$)

Calculate the residence time of O_2 in the mixed layer with respect to the "piston velocity" flux of O_2. ($22\ moles\ m^{-2} / 748\ mmol\ m^{-2}\ day^{-1} = 27.4$ days)

(8) A recent paper reported data for the gas nitrous oxide (N_2O) in the surface waters of the Arabian Sea (Lal and Patra, 1998, Global Biogeochemical Cycles, 12, 321-327). The average partial pressure of N_2O in the atmosphere over the Arabian Sea was 0.313 ppmv.
The Henry's Law constant for N_2O solubility at 25°C is $K_H = 25.7 \times 10^{-3}$ mol l^{-1} atm^{-1}.

a. What was the mean saturated concentration of N_2O in surface water at 25°C in mol l^{-1}.

8.04×10^{-9} mol/l

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.

The concentration is: 10.45×10^{-9} mol/l = 10.45×10^{-12} mol cm^{-3}
-22.7 cm/hr^{1}x (8.04×10^{-12} mol/cm^3-10.45×10^{-12} mol/cm^3) = 54.7×10^{-12} mol cm^{-2} $hour^{-1}$

(9) During our recent cruise to the Santa Barbara Basin the surface O_2 was 300 µmol 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?

Important information:
assume 1 l = 1 kg
atmospheric $P_{O2} = 0.20$
Henry's Law constant for O_2 in seawater at 25°C = 1.03×10^{-3} mol l^{-1} atm^{-1}
molecular diffusion coefficient for O_2 at 25°C = 2.0×10^{-5} cm^2 sec^{-1}
the film thickness = 50 µm = 5×10^{-3} cm

The flux is out; d/z = 4×10^{-3} cm sec^{-1}
Cs-C = 94×10^{-3} µmol cm^{-3}
Flux = 3.76×10^{-4} µmol cm^{-2} sec^{-1}

(10) You have measured O_2 and Ar concentrations in the surface ocean over the course of a month during the summer. Average water temperature and salinity were 25°C and 35ppt respectively for the period of observation. Average O_2 and Ar concentrations were 225 µmoles/kg and 10.7 µmoles/kg respectively. Both concentrations appeared to be at steady state.

a. Calculate the % saturation for O_2 and Ar in the surface layer at your site.

215µmoles/kg and 10.5 µmoles/kg respectively; 104.6% and 101.9% saturation.

b. Calculate the air-sea gas exchange using the stagnant boundary layer model. Assume that $D_{O2} = 2.3 \times 10^{-5}$ cm^2 s^{-1}, $D_{Ar} = 1.7 \times 10^{-5}$ cm^2 s^{-1} , and z (the stagnant boundary layer thickness) = 30µm.

for Ar : 1.14×10^{-6} µmol cm^2 sec^{-1} for O_2 : 76.6×10^{-6} µmol cm^2 sec^{-1}

c. Determine the magnitude of the bubble injection term for Ar and from that calculate the bubble injection for O_2. You can assume that bubble injection introduces gases into the ocean in the same proportions as they have in air.

For Ar this will be 1.14×10^{-6} µmol cm^2 sec^{-1} for O_2 this should be multiplied by oxygen/argon ratio (22.5) which yields 25.65×10^{-6} µmol cm^2 sec^{-1}

d. Determine the magnitude of the biological oxygen signal.

76.6×10^{-6} µmol cm^2 sec^{-1} - 25.65×10^{-6} µmol cm^2 sec^{-1} = 50.95×10^{-6} µmol cm^2 sec^{-1}

What processes influence surface water oxygen super saturation?

Seasonal warming
Air Injection (bubbles)
Net biological O_2 production

(11) You have two water beakers of 1 liter each one is at 0 degrees and the other at 30 degrees they are equilibrated with the atmosphere what is the nitrogen concentration in each? Now you mix these water masses and have 2 liters of mixture. What is the temperature? What is the N_2 concentration (no degassing occurred)? What is the degree of saturation of your mixture? Explain why? Where or when in the ocean would you expect this to happen?

N_2 14.3 ml/L and 7.82 ml/L respectively after mixing the temp is 15 degrees and N_2 is 11.06; The equilibrium value at 15 degrees should be 10.27 e.g. supersaturated ~7.7% This happens because the temp dependence of K_H is not linear with temp. Such change can happen during turbulent mixing of water masses with different temperatures (vents) also when seasonal temperature changes occur and the water has not equilibrated yet.