

## Chemistry 301 - Problem Set 1 - Answers

- 1) Describe the seasonal temperature-driven cycles of water that occur in many temperate lakes. Explain why this occurs, and what impact this has on the nutrients and dissolved gasses in these lakes.

Temperate lakes "turnover" twice a year when the density of the surface waters increases by either heating (springtime) or cooling (autumn) toward the temperature of maximum density (4°C). At these times, the surface waters are as dense (or more dense momentarily) than the waters beneath them, and they are able to sink down and/or mix with the deeper waters. This re-supplies nutrients to the surface waters and oxygen to the deep waters. Freshwaters have a temperature of maximum density above the freezing point because of the hydrogen bonds which form between water molecules. The large number of hydrogen bonds which form at temperatures less than 4°C leads to the formation of open tetrahedral structures which are less dense than the water is at warmer temperatures. (The extreme case is ice, which is much less dense than liquid water). Tropical lakes do not turn over since they never get below the temperature of maximum density, and will therefore always have warmer water on top of colder water.

- 2) What is the residence time of water in a lake with a volume of  $1.51 \times 10^{11}$  litres, two rivers flowing out of the lake at rates of  $6.12 \times 10^5$  l/hr and  $1.89 \times 10^4$  l/hr, and an evaporation rate of 1.4 l/hr? What happens to the residence time if a hot day increases the evaporation rate by a factor of 3?

$$\begin{aligned}\tau &= \frac{\text{Inventory}}{\text{rate of removal}} = \frac{(1.51 \times 10^{11}) \text{ litres}}{(6.12 \times 10^5 + 1.89 \times 10^4 + 1.4) \text{ litres/hr}} \\ &= \frac{(1.51 \times 10^{11}) \text{ litres}}{(6.31 \times 10^5) \text{ litres/hr}} = 2.39 \times 10^5 \text{ hours} = 9.97 \times 10^3 \text{ days} = \mathbf{27.3 \text{ years}}\end{aligned}$$

**Increasing the rate of evaporation by a factor of 3 makes no difference to the calculated residence time**, as this loss is not significant compared to the river outflow.

- 3) *Dry air is 20.95% O<sub>2</sub> by volume. If air at 1.0000 atm pressure is equilibrated with fresh water at 25°C, what is the partial pressure of O<sub>2</sub> in the water? What is the concentration of O<sub>2</sub> in the water? If water from the surface of a lake is measured to have 285 μM O<sub>2</sub> at 1.0000 atm and 25°C, what explanation(s) might you propose to explain this?*

Partial Pressure, P<sub>O<sub>2</sub></sub> at equilibrium in water =  $\chi_{O_2} * P_T$

where  $\chi_{O_2}$  = mole fraction of O<sub>2</sub> = (20.95%)/100 = 0.2095

and P<sub>T</sub> = total pressure = 1.0000 atm

But, need correction for water vapour since mole fraction is given for dry air, so:

$$P_{O_2} = (0.2095) (1.0000 \text{ atm} - 0.0313 \text{ atm}) = 0.2029 \text{ atm}$$

Henry's Law:  $[O_{2(aq)}] = K_H * P_{O_2}$  where K<sub>H</sub> = Henry's Law constant,

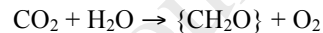
given in lecture as  $1.28 \times 10^{-3}$  mole/L.atm at 25°C

$$[O_{2(aq)}] = (1.28 \times 10^{-3} \text{ mole/L.atm}) \times (0.2029 \text{ atm})$$

$$[O_{2(aq)}] = 2.60 \times 10^{-4} \text{ mole/L} = \mathbf{260\mu M}$$

The observed O<sub>2</sub> concentration, 285 μM, is higher than the expected equilibrium concentration calculated above, 260 μM. This means that the **water is supersaturated with O<sub>2</sub>**. There are several possible explanations:

- 1) Excess photosynthesis (relative to respiration) leads to O<sub>2</sub> formation:



A recent or ongoing phytoplankton bloom could have added (or be adding) O<sub>2</sub> to the water faster than it can escape to the atmosphere, leading to a supersaturation.

- 2) The water could recently have been warmed, causing the equilibrium concentration of all gases to be lowered (T↑, K↓). Since it takes time for the gases to re-equilibrate with the atmosphere, there would be a temporary supersaturation. (That is, when the water was previously cooler, the equilibrium concentration would have been higher, perhaps the value that is currently observed).

- 3) "Bubble injection", resulting from recent stormy (windy) weather which leads to "white caps" on the surface of the water, and bubbles being mixed down deeper in the water. This means the water equilibrates with the atmosphere at higher pressures than exists at the surface of the water (bubbles get carried down to depth where the pressure is higher). At higher pressure, the equilibrium concentration is higher, so more gases can be dissolved in the water than you would expect if you only considered equilibration at the surface.

- 4) Calculate the total  $\text{CO}_2$  concentration (micromolar) in a solution of pH 6.5, in equilibrium with atmospheric  $\text{CO}_2$  at 400 ppm. How does this change if the atmospheric  $\text{CO}_2$  rises to 500 ppm (assuming the pH is still 6.5)? (Note: "atmospheric  $\text{CO}_2$  at 400 ppm" means  $P_{\text{CO}_2} = 400 \times 10^{-6} \text{ atm}$ )

Remember that  $\text{Total CO}_2 = [\text{CO}_2(\text{aq})] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$ .

First determine  $[\text{CO}_2(\text{aq})]$  using Henry's Law, then determine  $[\text{HCO}_3^-]$  from the  $K_{a1}$  equilibrium expression, and  $[\text{CO}_3^{2-}]$  from the  $K_{a2}$  equilibrium expression (or note that at pH 6.5  $[\text{CO}_3^{2-}]$  is going to be insignificant, as  $\text{pH} \ll \text{p}K_{a2}$ ).

$$\begin{aligned} P_{\text{CO}_2} &= (\text{mole fraction}) \times (\text{total pressure with correction}) \\ &= (400 \times 10^{-6} \text{ atm}) \times (1 \text{ atm} - 0.0313 \text{ atm}) \\ &= 387 \times 10^{-6} \text{ atm} \end{aligned}$$

$$\begin{aligned} [\text{CO}_2(\text{aq})] &= K_H * P_{\text{CO}_2} = (3.38 \times 10^{-2} \text{ mole/L atm}) (387 \times 10^{-6} \text{ atm}) \quad (\text{at } 25^\circ\text{C}) \\ &= \mathbf{1.31 \times 10^{-5} \text{ M}} \end{aligned}$$

$$\text{At pH 6.5, } [\text{H}^+] = 3.16 \times 10^{-7} \text{ M}$$

$$K_{a1} = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{CO}_2(\text{aq})]} = 4.47 \times 10^{-7}$$

$$[\text{HCO}_3^-] = K_{a1} \frac{[\text{CO}_2(\text{aq})]}{[\text{H}^+]} = \frac{(4.47 \times 10^{-7})(1.31 \times 10^{-5})}{(3.16 \times 10^{-7})} = \mathbf{1.85 \times 10^{-5} \text{ M}}$$

$$K_{a2} = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]} = 4.47 \times 10^{-11}$$

$$[\text{CO}_3^{2-}] = K_{a2} \frac{[\text{HCO}_3^-]}{[\text{H}^+]} = \frac{(4.47 \times 10^{-11})(1.85 \times 10^{-5})}{(3.16 \times 10^{-7})} = \mathbf{2.62 \times 10^{-9} \text{ M}}$$

$$\begin{aligned} \text{Total CO}_2 &= [\text{CO}_2(\text{aq})] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \\ &= 1.31 \times 10^{-5} + 1.85 \times 10^{-5} + 2.62 \times 10^{-9} = 3.16 \times 10^{-5} \text{ M} = \mathbf{31.6 \times 10^{-6} \text{ M} = 31.6 \mu\text{M}} \end{aligned}$$

Note that  $[\text{CO}_3^{2-}]$  is not significant, just as we presumed at the start, and can be excluded from the calculation.

If atmospheric  $\text{CO}_2$  rises to 500 ppm, the same calculation gives

$$\text{Total CO}_2 = \mathbf{4.00 \times 10^{-5} \text{ M} = 40.0 \mu\text{M}}$$