

Chemistry 301 - PROBLEM SET 1 - ANSWERS

- 1) *Describe the seasonal temperature driven cycles of water which occur in many temperate lakes. Explain why this occurs.*

Temperate lakes "turnover" twice a year when the density of the surface waters increases by either heating (springtime) or cooling (autumn) to the temperature of maximum density (4°C). At these times, the surface waters are as dense or more dense 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).

- 2) *What is the residence time of water in a lake with a volume of 1.51×10^{11} litres, two rivers flowing out of the lake at rates of 6.12×10^5 l/hr and 1.89×10^4 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% O₂ by volume. If air at 1.0000 atm pressure is equilibrated with fresh water at 25°C, what is the partial pressure of O₂ in the water? What is the concentration of O₂ in the water? If water from the surface of a lake is measured to have 285 μM O₂ at 1.0000 atm and 25°C, what explanation(s) might you propose to explain this?*

Partial Pressure, P_{O₂} at equilibrium in water = $\chi_{O_2} * P_T$

where χ_{O_2} = mole fraction of O₂ = (20.95%)/100 = 0.2095

and P_T = total pressure = 1.0000 atm

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

P_{O₂} = (0.2095) (1.0000 atm - 0.0313 atm) = 0.2029 atm

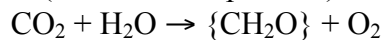
Henry's Law: [O_{2(aq)}] = K_H * P_{O₂} where K_H = Henry's Law constant,
given in lecture as 1.28 x 10⁻³ mole/L.atm at 25°C

[O_{2(aq)}] = (1.28 x 10⁻³ mole/L.atm) x (0.2029 atm)

[O_{2(aq)}] = 2.60 x 10⁻⁴ mole/L = **260μM**

The observed O₂ concentration, 285 μM, is higher than the expected equilibrium concentration calculated above, 260 μM. This means that the **water is supersaturated with O₂**. There are several possible explanations:

- 1) Excess photosynthesis (relative to respiration) leads to O₂ formation:



A recent or ongoing phytoplankton bloom could have added (or be adding) O₂ 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) (*Optional*) "Bubble injection", resulting from windy weather and white caps on the surface of the water, causes water to equilibrate with the atmosphere at higher pressures than exist 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 (P↑, K↑), 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 CO_2 concentration (micromolar) in a solution of pH 6.5, in equilibrium with atmospheric CO_2 at 390 ppm. How does this change if the atmospheric CO_2 rises to 500 ppm (assuming the pH is still 6.5)? (Note: "atmospheric CO_2 at 390 ppm" means $P_{\text{CO}_2} = 390 \times 10^{-6} \text{ atm}$)

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 $\text{pH} \ll \text{p}K_{a2}$).

$$[\text{CO}_2(\text{aq})] = K_H * P_{\text{CO}_2} = (3.38 \times 10^{-2} \text{ mole/L atm}) (390 \times 10^{-6} \text{ atm}) \quad (\text{at } 25^\circ\text{C})$$

$$= \mathbf{1.32 \times 10^{-5} \text{ M}}$$

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

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

$$[\text{HCO}_3^-] = K_{a1} \frac{[\text{CO}_2(\text{aq})]}{[\text{H}^+]} = \frac{(4.47 \times 10^{-7})(1.32 \times 10^{-5})}{(3.16 \times 10^{-7})} = \mathbf{1.86 \times 10^{-5} \text{ M}}$$

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

$$[\text{CO}_3^{2-}] = K_{a2} \frac{[\text{HCO}_3^-]}{[\text{H}^+]} = \frac{(4.47 \times 10^{-11})(1.86 \times 10^{-5})}{(3.16 \times 10^{-7})} = \mathbf{2.64 \times 10^{-9} \text{ M}}$$

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

$$= 1.32 \times 10^{-5} + 1.86 \times 10^{-5} + 2.64 \times 10^{-9} = \mathbf{3.18 \times 10^{-5} \text{ M}}$$

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 CO_2 rises to 500 ppm, the same calculation gives

$$\text{Total CO}_2 = \mathbf{4.07 \times 10^{-5} \text{ M}}$$