**Calculation Summary**

The concentration of gasi dissolved in the original water sample (mol L-1) is calculated from a mass balance of the measured headspace mixing ratio of gasi (ppmv), the calculated concentration in the equilibrated headspace water, and the volumes of the headspace water and headspace gas. The calculations also require the pressure of the headspace equilibration (assumed to be equal to barometric pressure during sampling), the temperature of the headspace equilibration (assumed to be equal to the water temperature), the universal gas constant (R), and the Henry’s Law Solubility Constant corrected to the temperature of the headspace equilibration system (assumed to be equal to the water temperature).

1. The following applies to gasi, where gasi is equal to CH4, N2O, or CO2:
   1. The gas constant (R), is
   2. The dissolved gas concentration in the original water sample is calculated from a mass balance of the headspace equilibration system:

where is the concentration of gasi dissolved in the original water sample, is the total moles of gasi dissolved in the original water sample, is the total moles of gasi in the equilibrated headspace gas, is the moles of gasi in the equilibrated water sample, and is the moles of gasi in the gas used for the headspace equilibrium. If a pure gas, such as helium or nitrogen, is used as the headspace gas, then = 0. If a mixed gas, such as ambient air, is used as the headspace gas, the term corrects the calculation for any amount of gasi contained in the headspace gas. Finally, is the volume of the original water sample.

* 1. is calculated from the Ideal Gas Law . In this equation, P = partial pressure of gasi and T is the temperature of the headspace equilibration system (assumed to be equal to water temperature).

Where is the measured mixing ratio of gasi in the equilibrated headspace gas, BP is barometric pressure (kPa), is the volume of gas used in the headspace equilibrium (mL), and T is the temperature of the headspace system (assumed to be equal to water temperature; K). 10-6 is a constant used to convert ppmv to parts.

* 1. is calculated from the Ideal Gas law, as above:

where is the measured mixing ratio of gasi in the pure headspace gas (i.e. before mixing with the water sample).

* 1. is calculated from Henry’s Law and the volume of water used in the headspace equilibration. Henry’s Law states that the concentration of gasi dissolved in a water sample is equal to the product of the partial pressure of gasi in the overlying atmosphere (i.e. the headspace gas) and the Henry’s Law Solubility Constant for gasi at the temperature of the water (H(T)).

In this equation, the partial pressure of gasi in the headspace gas is calculated as where 10-6 is a constant used to convert ppmv to parts. H(T) is obtained from the compilation of Sander (2015) (see below).

* 1. Sander (2015) provides a compilation of Henry’s Law Solubility Constants standardized to 298.15K. This standardized Henry’s Law Solubility Constant (HƟ) can be converted to the temperature of the headspace equilibration H(T) following:

where the term is equal to the constant provided in column in Table 6 of Sander (2015). This constant is equal to 2400 K, 1900 K, an d 2700 K for CO2, CH4, and N2O, respectively.

* 1. The full equation for calculating the concentration of gasi dissolved in the original water is: