

## Appendix B Calculation of $p_{O_2}$ in Water Equilibrated with a Mixture of Room Air and Nitrogen

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When gas A is dry air and mixed with an oxygen-free dry gas or gas mixture B (e.g.,  $N_2$ ), then the  $p_{O_2}$  in water equilibrated with this gas mixture is

$$p_{O_2} = ({}_b p - p_{H_2O, T_s}) \times \phi_A \times \phi_{O_2}^* \quad (1)$$

where  ${}_b p$  is barometric pressure [kPa],  $p_{H_2O, T_s}$  is the saturation water vapor pressure at the temperature of the water sample,  $\phi_A$  is the volume fraction of gas A in the gas mixture leaving the gas mixing pump,

$$\phi_A = \frac{p_A}{{}_b p} \text{ and } 1 - \phi_A = \frac{p_B}{{}_b p} \quad (2)$$

$\phi_{O_2}^*$  is the volume fraction of oxygen in dry air which can be taken as constant

$$\phi_{O_2}^* = 0.20946.$$

It may be more convenient to use room air instead of dry air. Then gas A contains water vapor proportional to the relative humidity,  $r_h$ , of room air,

$$p_{H_2O, A} = r_h \times p_{H_2O, T_A} \quad (3)$$

where  $p_{H_2O, A}$  is the water vapor pressure in room air, and  $p_{H_2O, T_A}$  is the saturation water vapor pressure at room temperature. The  $p_{O_2}$  in room air is therefore a function of  $r_h$  and  $T_A$ ,

$$p_{O_2, A} = ({}_b p - p_{H_2O, A}) \times \phi_{O_2}^* \quad (4)$$

According to Eq. (2), the water vapor pressure and oxygen pressure respectively in the gas mixture leaving the pump are

$$p_{H_2O, M} = \phi_A \times p_{H_2O, A} \quad (5)$$

and

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$$p_{O_2, M} = \phi_A \times p_{O_2, A} \quad (6)$$

We cannot apply Eq. (1) if  $p_{H_2O, M} > 0$ .

To derive the appropriate algorithm we may regard room air as a mixture of three components,

$${}_b p = p_{X, A} + p_{H_2O, A} + p_{O_2, A} \quad (7)$$

and we may express the pressure of the fraction of air not containing water vapor and oxygen,  $p_{X, A}$ , by combining Eqs. (4, 7),

$$p_{X, A} = ({}_b p - p_{H_2O, A}) \times (1 - \phi_{O_2}^*) \quad (8)$$

The pressure of gas not containing water vapor and oxygen in the gas mixture leaving the pump is

$$p_{X, M} = p_B + \phi_A \times p_{X, A} \quad (9)$$

Recalling Eq. (2),

$$p_B = (1 - \phi_A) \times {}_b p \quad (10)$$

and inserting Eqs. (8, 10) into (9) yields after rearrangement

$$p_{X, M} = {}_b p \times (1 - \phi_A \times \phi_{O_2}^*) - p_{H_2O, A} \times \phi_A \times (1 - \phi_{O_2}^*) \quad (11)$$

The total pressure in the gas phase leaving the pump is then

$${}_b p = p_{X, M} + p_{H_2O, M} + p_{O_2, M} \quad (12)$$

What is the  $p_{O_2}$  after saturating this gas mixture with water vapor at  $T_s$ ? When the water vapor pressure is brought from  $p_{H_2O, M}$  to  $p_{H_2O, T_s}$  then the total pressure remains constant, hence

$${}_b p = (p_{X, M} + p_{O_2, M}) \times x + p_{H_2O, T_s} \quad (13)$$

and

$$x = \frac{{}_b p - p_{H_2O, T_s}}{p_{X, M} + p_{O_2, M}} = \frac{{}_b p - p_{H_2O, T_s}}{{}_b p - p_{H_2O, A} \times \phi_A} \quad (14)$$

[see Eqs. (4, 6, 11) for obtaining the second expression]. The  $p_{O_2}$  in solution equals

$$p_{O_2} = p_{O_2, M} \times x \quad (15)$$

Inserting Eqs. (4, 6, 14) in Eq. (15) we finally get

$$p_{O_2} = ({}_b p - p_{H_2O, T_s}) \times \phi_A \times \phi_{O_2}^* \times \frac{{}_b p - p_{H_2O, A}}{{}_b p - p_{H_2O, A} \times \phi_A} \quad (16)$$

Thus we derived a correction factor,  $f_r$  for Eq. (1)

$$f_r = \frac{b^p - p_{H_2O,A}}{b^p - p_{H_2O,A} \times \phi_A} = 1 - p_{H_2O,A} \times \frac{1 - \phi_A}{b^p - p_{H_2O,A} \times \phi_A}. \quad (17)$$

$f_r$  equals 1 when  $\phi_A = 1$ , i.e., for saturation with water saturated air [Eq. (1)]. Since  $b^p \gg p_{H_2O,A} \times \phi_A$ , we may neglect the term  $p_{H_2O,A} \times \phi_A$  in Eq. (17) to obtain the simple approximation

$$f_r \approx 1 - p_{H_2O,A} \times \frac{1 - \phi_A}{b^p} = 1 - \phi_{H_2O,A} \times \phi_B. \quad (18)$$

Equation (18) approximates  $f_r$  to better than 1% for low volume fractions of air,  $\phi_A < 0.4$ , or high volume fractions of gas B,  $\phi_B > 0.6$ . This shows that the correction factor,  $f_r$ , is linearly dependent upon the volume fraction of water vapor in air,  $\phi_{H_2O,A}$ , and the relative volumes of the two gases mixed by the pump.

In practice this means that the error encountered by neglecting the correction factor for Eq. (1) increases with room temperature and relative humidity of air. It becomes relatively more important when working at low air saturations, and increases slightly with altitude (with decreasing barometric pressure). Under normal laboratory conditions and at air saturations set below 50%, errors from 1% to 3% result from disregarding  $f_r$  (Fig. 1). Hence the significance of the correction for  $p_{H_2O,A}$  is similar to that of the correction for  $p_{H_2O,T_s}$  in Eq. (1) which is generally accounted for.

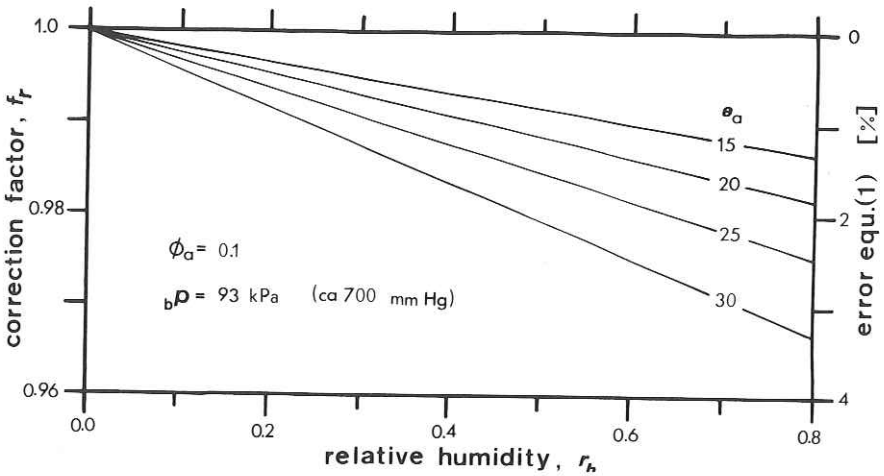


Fig. 1. Correction factor for Eq. (1),  $f_r$ , and error of Eq. (1) as a function of relative humidity of room air,  $r_h$ , and room temperature (numbers in  $^\circ\text{C}$ ) when 10% room air is mixed with 90% of an oxygen-free dry gas