ppmv

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In discussions of the carbon dioxide content of the atmosphere, the relative abundance of CO_2 is usually given in ppmv, or "parts per million by volume." I wrote these rather simple-minded notes in an effort to understand what ppmv really means, and how it relates to the mass fraction.

A mole is a quantity of substance corresponding to Avogadro's number of the atoms, molecules, electrons, or other discrete, fungible entities of which the substance is composed. Avogadro's number is 6.0221415×10^{23}.

Consider a substance denoted by subscript i. The molar mass of the substance, M_i, is defined as the mass of one mole of the substance. The molar mass is also called the molecular weight – a bad name, because it's really mass, not weight. The total mass of the substance is the number of moles times the mass of one mole: $n_i M_i$.

The molar volume, V, is defined to be the volume occupied by one mole of the substance, *at a standard temperature and pressure* (hereafter STP), which are usually taken as $p_{\text{standard}} = 100$ kPa and $T_{\text{standard}} = 0°$C. We demonstrate below that the molar volume is the same for all ideal gases, which is why it doesn't need a subscript.

The ideal gas law can be written as

$$p_i v = n_i R^* T \ , \tag{1}$$

where p_i is the partial pressure of species i; v is the volume occupied, assumed to be the same for all species; n_i is number of moles present; $R^* \cong 8.31$ J K^{-1} mol^{-1} is the universal gas constant; and T is the temperature, which is assumed to be the same for all species. For the special case of one mole at STP, we know that $v = V$ and $n_i = 1$. Then (1) reduces to

$$p_{\text{standard}} V = R^* T_{\text{standard}} \tag{2}$$

which can be rearranged to

$$V = R^* T_{\text{standard}} / p_{\text{standard}} \ . \tag{3}$$

It follows from (3) that, as mentioned above, the molar volume is the same for all ideal gases. With the numerical values of the standard pressure and temperature given above, it turns out that $V = 2.27 \times 10^{-2}$ m^3 mol^{-1}.

Now let's define three fractions. The mole fraction of species i is

$$(\text{mole fraction})_i \equiv n_i / \sum_{j=1}^{N} n_j \ , \tag{4}$$

where N is the total number of species present. The mass fraction of species i is

$$(\text{mass fraction})_i \equiv n_i M_i / \sum_{j=1}^{N} n_j M_j \ . \tag{5}$$

Finally, the fractional pressure of species i is

$$\begin{aligned}(\text{fractional pressure})_i \equiv & p_i / \sum_{j=1}^{N} p_j \\ = & n_i / \sum_{j=1}^{N} n_j \ .\end{aligned} \tag{6}$$

The second line of (6) is obtained using our assumptions that all of the gases occupy the same volume and have the same temperature. It shows that the fractional pressure is equal to the mole fraction.

At STP, the volume fraction reduces to

$$\begin{aligned}(\text{volume fraction})_i \text{ at STP} = & n_i V / \sum_{j=1}^{N} n_j V \\ = & n_i / \sum_{j=1}^{N} n_j \ ,\end{aligned} \tag{7}$$

which is the same as the mole fraction. *This equality of the mole fraction and volume fraction applies only at STP*. Although the mole fraction expressed in parts per million is often referred to as “parts per million by volume,” or ppmv, this is true only at STP.

The total atmospheric mass of “dry air” is about 5.123 x 10^{21} g (Trenberth et al. 1987). The effective molecular weight of dry air is $M_{\text{dry air}} = 28.9$ g mol^{-1}. It follows that the atmosphere consists of 1.77 x 10^{20} moles of dry air.

The total mass of atmospheric water vapor varies seasonally but is about 1.22 x 10^{19} g in the annual mean. The molecular weight of water vapor is 18 g mol^{-1}. It follows that the atmosphere consists of 6.78 x 10^{17} moles of water vapor.

Considering dry air and water vapor together, the mass of the atmosphere is about 5.1361 x 10^{21} g, and the number of moles is about 1.78 x 10^{20}. The mole fraction of water vapor is 3809 ppmv.

The molecular weight of CO_2 is 44 g mol^{-1}. The current (April 2023) CO_2 content of the atmosphere is about 410 ppmv, or 420 x 10^{-6} moles per mole. The atmosphere contains about 7.48 x 10^{16} moles of CO_2. The number of moles of CO_2 is thus about 1/9 the number of moles of of water vapor. The total mass of CO_2 is about 3.29 x 10^{18} g.

The mass of water vapor is thus about 3.7 times larger than the mass of CO_2.

Reference

Trenberth, K. E., J. R. Christy, and J. G. Olson, 1987: Global atmospheric mass, surface pressure, and water vapor variations. *Journal of Geophysical Research: Atmospheres*, **92 (D12)**, 14 815–14 826.