2.1 Altering the atmosphere / ppmv and factorisation

This week we introduce the concept of volumetric mixing ratio, which is expressed using the 'parts-per' notation (e.g. parts per million by volume, ppmv). In atmospheric science ppmv is used in describing the concentrations of pollutants in air. Lets start with the ideal gas law:

$$PV = NR_{gas}T$$

where P is the total pressure (units of pascals); V the volume of the gas (units of m^3); N the number of moles of gas; $R_{gas} = 8.314\, J\, K^{-1}\, mol^{-1}$ the universal gas constant; T the temperature of the gas (units of kelvin).

Questions on ideal gas law:

1. Calculate how many moles of air there are in a container of volume 2 m^3 at $P = 1000$ hPa (h=hecto$\equiv 1 \times 10^2$) and $T = 290$ K.
2. How many molecules is that? (Avogadros number, $N_A = 6.02 \times 10^{23}$).
3. Work out the volume that 1 mole of *any gas* occupies at $P = 1000$ hPa; $T = 273.15$ K (so called standard temperature and pressure). Give your answer in litres.

Dalton's law of partial pressure

When the volume of gas contains several different gases (as in air for example) each gaseous component is said to exert a *partial pressure* that contributes to the total pressure. This is *Dalton's law of partial pressures*.

$$p_iV = N_iR_{gas}T$$

where p_i is the partial pressure of component i; N_i is the number of moles of component i and other terms have been defined above.

Each gaseous component is said to exert a partial pressure because the total pressure is equal to the sum of the partial pressures:

$$P = p_1 + p_2 + \cdots + p_n$$

Questions on Dalton's law of partial pressures:

By mole, air contains roughly 21% molecular oxygen (O_2), 78% molecular nitrogen (N_2). Let us say that the remaining 1% is carbon dioxide (CO_2, not true in natural air).

1. Consider the 2 m^3 container ($P = 1000$ hPa; $T = 290$ K) with the same number of moles of the air described above that you calculated in the first question on *ideal gas law*. How many moles of oxygen, nitrogen and carbon dioxide are there?
2. Using Dalton's law of partial pressures, calculate the partial pressures of each component and the total pressure by summing them up. Is it what you expected?

Concentrations using the 'parts-per' notation

Concentrations of pollutants / trace gases in the atmosphere are often expressed using the 'parts-per' notation (e.g. parts-per million; parts-per billion, etc). This is actually a *volumetric mixing ratio*.

Volumetric mixing ratio means that if you were to consider the pollutant to be at the *same* temperature and pressure as all of the gaseous components the ratio of the volume of the gaseous pollutant to the volume of all of the gaseous components would be the volumetric mixing ratio.

If we consider a mixture of gases in a room at some P and T we can think of each gaseous component of the mixture occupying a 'partial volume', V_i. The ideal gas law is then:

$$PV_i = N_i R_{gas} T$$

where P is the total pressure; V_i is the 'partial volume' (some fraction of the total volume); N_i is the number of moles of component i.

Also, the sum of the moles of each component equals the total number of moles of gas:

$$N = N_1 + N_2 + \cdots + N_n$$

and the sum of partial volumes equals the total volume:

$$V = V_1 + V_2 + \cdots + V_n$$

This is a confusing way to think about things! The reasons being that the partial pressure of the pollutant is, in general, not equal to the pressure of all of the gaseous components, and if the gases are 'well mixed' the physical volume that the pollutant occupies is the same as the volume of the rest of the gases, so the ratio of volumes will be equal to unity.

Because *volume is only proportional to number of moles* for gases at the same *pressure and temperature* we can also describe the volumetric mixing ratio as the *number of moles of the pollutant* divided by the *number of moles of the rest of the gaseous components*. Dividing the equation for partial volume above by the ideal gas law we have:

$$\frac{\cancel{P}V_i}{\cancel{P}V} = \frac{N_i \cancel{R_{gas}T}}{N \cancel{R_{gas}T}}$$

and arrive at the result that the volumetric ratio is actually the ratio of the number of moles of the pollutant to the total number of moles. Why don't we just call it the molar ratio? I think it would make it easier to understand.

By taking the ratio of Dalton's law of partial pressures to the ideal gas law we find that the molar ratio is also the ratio of partial pressure to total pressure.

The volumetric ratio is multiplied by a large number (e.g. 1×10^6; or 1×10^9) to put it in parts per million or parts per billion, etc.

Questions on volumetric mixing ratio:
In a mixture of gases the number of moles of each of the components are $N_1 = 25$; $N_2 = 15$; $N_3 = 0.005$. The temperature is equal to $T = 290$ K and the total volume is 2 m^3.

1. Calculate the volumetric mixing ratio of component 3. Express the result in ppm.
2. Calculate the partial pressures of each component using Dalton's law of partial pressures, use these to calculate the total pressure. Thus calculate the ratio of the partial pressure of component 3 to the total pressure.
3. Using the total pressure calculate the 'partial volume' of each of the gaseous components and thus the volumetric ratio of component 3 in ppm.

Mass mixing ratios - no questions on this
Concentrations can also be expressed using the mass mixing ratio. This is the mass of pollutant divided by the mass of all other gaseous components.
To understand this concept, multiply the Dalton's law by the molecular weight, $M_{r,i}$, of the component being considered:

$$p_i V M_{r,i} = N_i M_{r,i} R_{gas} T$$

$N_i \times M_r$ is the mass of one of the gaseous components, m_i. Rearranging gives:

$$m_i = \frac{p_i V M_{r,i}}{R_{gas} T}$$

The mass mixing ratio is defined as:

$$\begin{aligned}\text{mass mixing ratio} &= \frac{m_i}{m_1 + m_2 + \dots m_n} \\ &= \frac{p_i V M_{r,i}/(R_{gas}T)}{p_1 V M_{r,1}/(R_{gas}T) + p_2 V M_{r,2}/(R_{gas}T) + \cdots + p_n V M_{r,n}/(R_{gas}T)} \\ &= \frac{p_i M_{r,i}}{p_1 M_{r,1} + p_2 M_{r,2} + \cdots + p_n M_{r,n}}\end{aligned}$$

in the last step we have *factorised* $\frac{V}{R_{gas}T}$ and cancelled it from the top and bottom. If you can't see how to do this step look at sections 2.5 and 2.9 of the *foundation maths support pack*.

Answers to questions on ideal gas law

1. 82.9511
2. 4.99×10^{25}
3. 22.7 litres.

Answers to questions on Dalton's law of partial pressure

1. 17.41, 64.70, 0.8295
2. The partial pressures of oxygen, nitrogen and carbon dioxide are: 2.1×10^4 Pa; 7.8×10^4 Pa; 0.1×10^4 Pa. The sum of the partial pressures is equal to the total pressure: 1×10^5 Pa. This should be equal to the total pressure from the given in the first question.

Answers to questions on volumetric mixing ratio

1. 125 ppm(v)
2. 3.01×10^4 Pa; 1.81×10^4 Pa; 6.03 Pa. The total pressure is 4.82×10^4 Pa. Thus the ratio of p_3 to P is 125 ppm(v).
3. 1.2498, 0.75, 0.0002 m^3. Total volume is 2 m^3. Volumetric mixing ratio: 125 ppm(v).