The Composition of Air

David Randall

Pressure is the normal component of the force per unit area exerted by fluid molecules. In an ideal fluid the pressure at a point is the same in all directions. Temperature is a measure of the kinetic energy of the random molecular motions.

A perfect gas is one that exactly obeys the laws of Boyle and Charles. Boyle's Law says that at a given temperature the pressure of a given mass of gas is inversely proportional to its volume. Charles' Law says that the volume of a gas at fixed pressure is directly proportional to its temperature. A gas that obeys both of these Laws satisfies the following equation of state:

$$p\alpha = R'T \, , \tag{1}$$

Here R' is the "specific" gas constant, which is associated with the particular type of gas. Avogadro found that 1 g molecular weight (mole) of *any* gas occupies 22400 cm^3 at temperature $T_0 = 273.15$ K (the freezing point of pure water), and pressure $p_0 = 1013.25$ hPa ("one atmosphere"). Obviously, this reference temperature and reference pressure have been arbitrarily chosen, and the particular volume measured, i.e. 22400 cm^3, depends on these choices. It follows that, for the particular case of $V_0 = 22400 \text{ cm}^3$, the equation of state becomes

$$p_0 V_0 = mR'T_0 \, , \tag{2}$$

where m is the molecular weight. Avogadro's discovery implies that there exists a *universal* gas constant:

$$R^* = mR' = \frac{p_0 V_0}{T_0} \, . \tag{3}$$

The equation of state can now be written as

$$p\alpha = \frac{R^*}{m} T \, . \tag{4}$$

As shown in Table 1, “dry air” is a mixture of nitrogen, oxygen, argon, carbon dioxide, etc., which are all, practically speaking, perfect gases, and so obey (4). The composition of dry air is nearly homogeneous below 20 km. Except for water vapor and ozone, whose concentrations vary greatly, the concentrations of the other principal constituents of the atmosphere, i.e., N_2, O_2, Ar, CO_2, Ne, He, Kr, H_2, CH_4, and N_2O, are nearly homogeneous up to about 80 km.

For a mixture of perfect gases occupying volume V at temperature T, Dalton's law states that:

- each gas completely occupies the volume;
- each gas obeys its own equation of state;
- the total pressure due to the mixture of gases is the sum of the partial pressures exerted by the individual gases.

Gas	Molecular Weight.	R’, J kg K^{-1}	Mass fraction of the “dry” portion of the atmosphere, in %
Nitrogen	28.016	296.7	75.52
Oxygen	32	259.8	23.15
Argon	39.444	208.1	1.28
Carbon Dioxide	44.01	188.9	0.06

Table 1: The composition of “dry air.”

Therefore,

$$p_i V = M_i R_i' T = M_i \frac{R^*}{m_i} T, \; i = 1,2, \; \ldots, \; n \, . \tag{5}$$

Here subscript i denotes a particular species, p_i is the partial pressure, M_i is the mass, R^* is the universal gas constant, and m is the molecular weight. It follows that

$$V \sum_{i=1}^{n} p_i = T \sum_{i=1}^{n} M_i R_i' = R^* T \sum_{i=1}^{n} \frac{M_i}{m_i} . \tag{6}$$

Using

$$p \equiv \sum_{i=1}^{n} p_i , \rho \equiv \sum_{i=1}^{n} \frac{M_i}{V} , M \equiv \sum_{i=1}^{n} M_i \ , \tag{7}$$

we find that

$$p = \rho R T \ , \tag{8}$$

where the effective gas constant of the mixture is

$$R \equiv \sum_{i=1}^{n} \frac{M_i R_i'}{M} = \sum_{i=1}^{n} \frac{M_i}{m_i} \ . \tag{9}$$

For dry air, $R = R_d \cong 287$ J kg^{-1}K^{-1}. The apparent molecular weight of dry air is

$$m_d = \frac{R^*}{R} \equiv 28.966 \ g \ \text{mole}^{-1}. \tag{10}$$

When the effects of moisture are included, (8) is often modified to use the gas constant for *dry* air, with a “virtual temperature.”