4. Perfect Gas Law

In this section we introduce some of the basic results of thermodynamics and apply them to some simple, but important atmospheric situations.

In the kinetic theory of gases, an *ideal* gas is one in which the individual molecules are sufficiently far apart that the short range force that acts between them can be ignored. Collisions between molecules are assumed to be perfectly elastic.

Laboratory experiments have shown that for such a gas there is a simple equation of state relating the pressure p, absolute temperature T, and volume V. For m kilograms of gas, this equation may be written

$$pV = mRT, \qquad (4.1)$$

where R is a constant for the particular gas. R is called the gas constant and has units of Joules per degree per kilogram.

We define a *kilogram-molecular* weight, or *kilomole* (abbreviated *kmole*) of a material as its molecular weight expressed in kilograms. (Older texts define *molecular weight* as the molecular weight expressed in grams). For example, the molecular weight of water is 18.016, and therefore one kilomole of water is 18.016 kg of water. The number of kilomoles n in mass m (in kilograms) of material is given by

$$n = m/M. \qquad (4.2)$$

Where M is the molecular weight. One kilomole of any material is equal to the weight of a single molecule (in kg) times the number of molecules, N. This number is called Avogadro's number and has the value 6.022×10^{26} (for a kmol of substance).

Avogadro hypothesized that gases containing the same number of molecules occupy the same volume at the same pressure and temperature. This implies that for one kilomole of any gas (i.e., $m = M$ from Eq. 4.2)

$$pV = MRT \qquad (4.3)$$

from Eq. (4.1). Accordingly, $R^* = MR$ is a universal constant for all gases. It is called the *universal gas constant* and has the value 8314.3 $J\, deg^{-1}\, kmol^{-1}$.

For n kmol of any gas, the ideal gas Eq. (4.1) takes the form

$$pV = n\,R^*T\,. \qquad (4.4)$$

Although air is a mixture of gases with different molecular weights, it is possible to define an apparent molecular weight so that Eq. (4.4) still applies to the mixture.

Consider 1 *kg* of *dry air* containing $m_i\ kg$ of the i-th constituent which has molecular weight M_i and exerts a partial pressure p_i. From Dalton's law of partial pressures, the total pressure of the gas mixture, $p = \sum p_i$. Since each component occupies the same volume *V*, and the number of kilomoles of the i-th component is m_i / M_i, Eq. (4.4) gives

$$p_i V = \frac{m_i}{M_i} R^* T,$$

and summation over *i* gives

$$pV = \left(\sum_i \frac{m_i}{M_i} \right) R^* T. \tag{4.5}$$

This has the same form as Eq. (4.4) if $n = \sum (m_i / M_i)$. Referring to Eq. (4.2), we see that it follows that the apparent molecular weight of the mixture

$$M_d = \sum_i m_i / (\sum_i m_i / M_i). \tag{4.6}$$

Note that the apparent molecular weight is not a simple arithmetic average of the constituent species. It makes sense to define an apparent molecular weight for dry air because the proportions of the constituents are very nearly constant.

The *specific volume* of the gas α, is the volume per unit mass (i.e., $V = \alpha$ when m =1). Note that $\alpha = 1/\rho$ where ρ is the density. For dry air, $M_d = 28.97$. Hence, Eq. (4.5) reduces to

$$p\alpha = R_d T, \quad or \quad p = \rho R_d T \tag{4.7}$$

where $$R_d = R^* / M_d = 287 J\, K^{-1} kg^{-1}.$$

A similar calculation can be carried out for moist air, regarding this as a mixture of dry air and water vapour.