The Ideal Gas Law: Application to the Atmosphere

For a sample of any ideal gas, the ideal gas law relating pressure, temperature, volume, and the number of molecules of the gas (expressed in moles), can be written as:

\[ pV = nR^*T \]

where \( p \) \equiv pressure exerted by the gas, \( V \equiv \) volume occupied by the gas, \( n \equiv \) number of moles of the gas, \( R^* \equiv \) universal gas constant, and \( T \equiv \) temperature of the gas. This relation applies both to single gases and to mixtures of gases.

For a mixture of gases (such as air), each gas exerts a partial pressure, \( p_i \) (where “\( i \)” is an index that identifies each gas in the mixture), and the total pressure exerted by the gas equals the sum of the partial pressures:

\[ p = \sum_{i=1}^{N} p_i \]

where \( N \) is the number of gases in the mixture.

The ideal gas law applies to each gas in the mixture separately, even when the gases are mixed together:

\[ p_iV = n_iR^*T \]

where \( n_i \equiv \) the number of moles of the \( i \)th gas. Of course, the total number of moles of gas in a mixture of gases is just the sum of the number of moles of each gas in the mixture:

\[ n = \sum_{i=1}^{N} n_i \]

The number of moles of a gas can be related to the mass of the gas, \( m_i \), and the molecular weight of the gas (expressed in terms of mass of the gas per mole), \( M_i \):

\[ n_i = \frac{m_i}{M_i} \]

Of course, the total mass of gas in a mixture, \( m \), is just the sum of the masses of the individual gases:

\[ m = \sum_{i=1}^{N} m_i \]

The number of moles of a gas mixture can be related to the total mass of the mixture and a weighted-mean molecular weight of the mixture, \( \overline{M} \):
(7) \( n = \frac{m}{M} \)

(It makes sense to use a weighted mean instead of a simple arithmetic mean because if one gas dominates the mixture, the molecular weight of the mixture should be more like that of the dominant gas than of any other gas.)

Now, if we sum both sides of (3) over all gases in the mixture, we can write:

\[
(8) \left( \sum_{i=1}^{N} p_i \right) V = \left( \sum_{i=1}^{N} n_i \right) R^* T
\]

Substituting (2) and (4) into (8) simply gives (1), as we’d expect, but if we substitute (5) instead of (4) into (8) we get:

\[
(9) \quad pV = \left( \sum_{i=1}^{N} \frac{m_i}{M_i} \right) R^* T
\]

If we substitute (7) and then (6) into (1), we get:

\[
(10) \quad pV = \frac{m}{\bar{M}} R^* T = \left( \sum_{i=1}^{N} m_i \right) \frac{R^*}{\bar{M}} T
\]

Equating the right-hand sides of (9) and (10), both of which equal \( pV \), gives:

\[
(11) \quad \left( \sum_{i=1}^{N} \frac{m_i}{M_i} \right) R^* T = \left( \sum_{i=1}^{N} m_i \right) \frac{R^*}{\bar{M}} T
\]

Solving (11) for \( \bar{M} \) gives us an expression for a weighted-mean molecular weight of a mixture of gases as it must be defined in the context of the gas law:

\[
(12) \quad \bar{M} \equiv \left( \sum_{i=1}^{N} m_i \right) / \left( \sum_{i=1}^{N} \frac{m_i}{M_i} \right)
\]

Substituting (6) and (12) into (10) gives:

\[
(13) \quad pV = m \left( \frac{R^*}{\bar{M}} \right) T
\]

Dividing both sides by \( V \) gives:

\[
(14) \quad p = \left( \frac{m}{V} \right) \left( \frac{R^*}{\bar{M}} \right) T = \rho \left( \frac{R^*}{\bar{M}} \right) T
\]

where \( \rho \) is the density of the gas mixture.

For the most part, the gases that constitute air are present in relatively fixed proportions to each other. The main exception is water vapor, which can exist in amounts varying from almost nothing to as much as \( \sim 4\% \) of the total number of molecules. The variability of water vapor vs. the relatively fixed proportions of the other gases has led meteorologists to define the
concept of “dry air”, which consists of air without considering the water vapor in it. For dry air, the ideal gas law can be written:

\[ p_d = \left( \frac{m_d}{V} \right) \left( \frac{R'}{M_d} \right) T \equiv \rho_d \left( \frac{R'}{M_d} \right) T \]  

where the subscript “d” refers to the dry air mixture. Considering the water vapor in addition to the dry air, applying the gas law, and applying (2) above, gives us a version of the gas law that can be written as:

\[ p = e + p_d = \left( \frac{m_v + m_d}{V} \right) \left( \frac{R'}{M} \right) T \equiv \left( \rho_v + \rho_d \right) \left( \frac{R'}{M} \right) T = \rho \left( \frac{R'}{M} \right) T \]

Where \( e \) is the partial pressure of water vapor. This is more useful for many atmospheric applications if \( M \) is rewritten in terms of \( M_d \). We can write the following, where \( N_d \) is the number of gases in the dry air mixture (so that \( N = N_d + 1 \)):

\[ M = \left( \sum_{i=1}^{N} m_i \right) / \left( \sum_{i=1}^{N} m_i / M_i \right) = \left( \sum_{i=1}^{N_d} m_i + m_v \right) / \left( \sum_{i=1}^{N_d} m_i / M_i + m_v / M_v \right) \]

\[ = (m_d + m_v) / \left( \sum_{i=1}^{N_d} M_i / M_d + m_v / M_v \right) \]

\[ = m_d (1 + m_v / m_d) \left[ m_d \left( \frac{1}{m_d} \sum_{i=1}^{N_d} m_i / M_i + m_v / m_d \right) \right] \]

\[ = (1 + m_v / m_d) \left[ \frac{1}{M_d} + m_v / M_v \right] \]

\[ = M_d (1 + m_v / m_d) \left[ 1 + \left( \frac{m_v}{m_d} \frac{M_v}{M_d} \right) \right] \]

\[ \equiv M_d (1 + w) / (1 + w / \epsilon) \]

where \( \epsilon \equiv M_v / M_d \) is a constant and \( w \equiv m_v / m_d \) is defined as the mixing ratio of the parcel.

Substituting (17) into (16) gives an alternative version of the ideal gas law for air containing water vapor:

\[ p = \rho \left( \frac{R'}{M_d} \right) \left( \frac{1 + w / \epsilon}{1 + w} \right) \frac{1}{T} \equiv \rho R_d \left( \frac{1 + w / \epsilon}{1 + w} \right) \frac{1}{T} \equiv \rho RT \]

where \( R_d \equiv R' / M_d \) is the gas constant for dry air, and the gas constant for moist air in (18) would be:
Because the gas constant, \( R \), depends on the mixing ratio, \( w \) (and hence the amount of water vapor in the air), it hardly seems like a constant. The variability of the gas constant based on the composition of the air is inconvenient for many purposes, so meteorologists have preferred to apply the factor \( (1 + w/\varepsilon)/(1 + w) \) in (18) to the temperature, \( T \), instead of \( R_d \) and define a “virtual temperature”, \( T_v \), so that the gas law becomes:

\[
(20) \quad p = \rho R_d T_v
\]

where the virtual temperature is:

\[
(21) \quad T_v \equiv \left( \frac{1 + w/\varepsilon}{1 + w} \right) T
\]

The virtual temperature has no particular physical meaning but is instead a mathematical convenience that allows us to use the gas constant for dry air, \( R_d \), in the gas law even when there is water vapor present.

It is possible to show from (2), (3) and (15) that

\[
(22) \quad w \equiv m_v/m_d = \varepsilon e/p
\]

Substituting (22) into (17) and manipulating algebraically gives:

\[
(23) \quad \overline{M} = M_d \left( 1 - \frac{e}{p} (1 - \varepsilon) \right)
\]

Substituting (22) into (18) and manipulating gives:

\[
(24) \quad p = \rho \left( \frac{R}{M_d} \right) T / \left( 1 - \frac{e}{p} (1 - \varepsilon) \right)
\]

so that an alternative (but equivalent) expression for the virtual temperature in terms of the total pressure, \( p \), and the partial pressure of water vapor, \( e \), is:

\[
(25) \quad T_v = \frac{T}{1 - \frac{e}{p} (1 - \varepsilon)}
\]