The Ideal Gas Law Applied to Moist Air

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In chemistry the ideal gas law combines Boyle's Law, which relates pressure to volume at a constant temperature (developed in the 1600's) and Charles' Law, which relates volume and temperature at constant pressure, (developed in the late 1700s):

$$(1) \quad pV = nR^*T$$

where p is the pressure exerted by the gas in a closed container, V is the volume of the container, n is the number of moles of the gas present in a closed container, R^* is the universal gas constant, and T is the absolute temperature of the gas. (R^* is essentially a constant of proportionality between pressure on the one hand and the product of $n \times T$ on the other hand, for any gas. R^* has dimensions of pressure/(moles $\times$ temperature), though moles are actually a dimensionless quantity—it's just a count, without units.

For applications outside the laboratory, such as in the atmosphere, we don't have a closed container, so Eq. (1) has limited practical value. Fortunately, we can modify it to become more useful to the Earth sciences.

To do this, we first consider a "parcel" of air in the atmosphere and introduce two quantities: the mass of the parcel (m) and the effective molecular weight of the mixture of gases in the parcel (M), which is a weighted sum of the molecular weights of the individual gases in the mixture (weighted by their respective masses). (Dry air—that is, air without water vapor in it--is mostly nitrogen [~78%] and oxygen [~21%], with a little bit of argon [~1%], a very small amount of carbon dioxide [~0.04%], and trace amounts of a number of other, more exotic compounds. Water vapor can be present in variable amounts, typically around 1% where we live but no more than about 4% by number of molecules.)

The molecular weight of a substance is the mass of the substance per mole of the substance. (A mole is Avogadro's number of molecules of the material.) Hence, the mass of a substance is just the number of moles of the substance times its molecular weight:

$$(2) \quad m = n \times M$$

If we solve Eq. (2) for the number of moles (n) and substitute into Eq. (1) (to eliminate the number of moles from the resulting equation), we get:

$$(3) \quad pV = \left(\frac{m}{M}\right)R^*T = m\left(\frac{R^*}{M}\right)T \equiv mRT$$

where R is a gas constant that is specific to the particular type of gas or mixture of gases in the parcel (that is, this gas constant isn't universal but depends on the composition of the gas, thanks to its dependence on the molecular weight of gas).

Now solve Eq. (3) for pressure:

$$(4) \quad p = \left(\frac{m}{V}\right)RT \equiv \rho RT$$

where $\rho = m/V$ is the density of the gas.

The form of the gas law in Eq. (4) ($p = \rho RT$) is written in a way that doesn't depend on the size of the parcel or the amount (mass) of material in it, and hence is potentially more useful for applications in the atmosphere. To be truly useful, though, we have to know what the gas constant is for air, and that can vary because the amount of water vapor in air varies from place to place and time to time, which means that the composition of air varies a little bit, which means that the gas constant for "moist" air—that is, air with water vapor in it—varies from place to place and time to time. That is, the gas constant for air isn't exactly constant because the composition of air isn't uniform or steady.

We won't go into the gory details here, but it's possible to show that the gas "constant", R, can be expressed in terms of the gas constant for dry air (that is, air with no water vapor in it), R_d (which really is constant because the composition of dry air is virtually the same throughout the atmosphere), and the water vapor mixing ratio, w, a measure of the amount of water vapor present in the air.

Water vapor mixing ratio is defined as follows:

$$(5) \quad w \equiv m_v/m_d$$

where m_d is the mass of "dry" air in a parcel and m_v is the mass of water vapor "mixed in" with the dry air. Mixing ratio is the mass-based fraction of water vapor in the air relative to the amount of dry air (the mass of water vapor present per unit mass of dry air).

The gas constant for air can be related to R_d and w as follows:

$$(6) \quad R = R_d \left(\frac{1+w/\varepsilon}{1+w}\right)$$

where $\varepsilon \equiv M_v/M_d$, and M_v is the molecular weight of water = 18.02 gm/mole and M_d is the (mass-weighted average) molecular weight of dry air = 28.96 gm/mole. (Hence, ε = (18.02 gm/mole)/(28.96 gm/mole) = 0.622.)

Finally, substituting Eq. (6) into Eq. (4) gives us the following version of the gas law for "moist" air:

$$\boxed{(7) \quad p = \rho R_d \left(\frac{1+w/\varepsilon}{1+w}\right) T}$$

The universal gas constant, R^* = 8.31445 Joules/mole/Kelvin, so

$$R_d = R^*/M_d = (8.31445 \text{ Joules/mole/K})/(28.96 \text{ gm/mole})$$

$$= (8.31445 \times 10^3 \text{ Joules/kmole/K})/(28.96 \text{ kg/kmole})$$

$$R_d = 287.1 \text{ J/kg/K}$$

(We've converted all units to MKS units here for consistency.)