

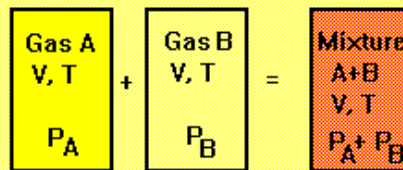
Lecture 4: Mixture of Ideal Gases

Dalton's Law: The total pressure exerted by a mixture of gases which do not interact chemically is equal to the sum of the partial pressures, where the partial pressure of a gas is the pressure exerted by this individual gas at the same temperature of the mixture if it alone occupies the same volume of the mixture.



The law was discovered by John Dalton in 1803. John Dalton (1766-1844) was a chemist and meteorologist, born in September 6, 1766 in Cumberland, England.

Dalton's Law of Partial Pressure: The **total pressure** of mixture of nonreacting gases is the sum of the **partial pressures** exerted by each of the gases in the mixture occupying the same volume at the same temperature.



For simplicity, let us consider a mixture of 2 gases only, Gas 1 and Gas 2. They have the following properties:

Gas 1: p_1, α_1, T, V

Gas 2: p_2, α_2, T, V

Based on Dalton's Law, the total pressure (p) is

$$p = p_1 + p_2, \quad (2.11a)$$

The equation of state for each gas can be written as

$$p_1 \alpha_1 = R_1 T = \left(\frac{R^*}{M_1} \right) T \quad \text{and}$$

$$p_2 \alpha_2 = R_2 T = \left(\frac{R^*}{M_2} \right) T$$

Since $\alpha_1 = 1/\rho_1 = V/m_1$; $\alpha_2 = 1/\rho_2 = V/m_2$, the above 2 equation can be rewritten as

$$p_1 = \left(\frac{R^* T}{V} \right) \left(\frac{m_1}{M_1} \right); \quad p_2 = \left(\frac{R^* T}{V} \right) \left(\frac{m_2}{M_2} \right)$$

Substituting p_1 and p_2 into Eq. (2.11a) leads to

$$p = p_1 + p_2 = \left(\frac{R^* T}{V} \right) \left(\frac{m_1}{M_1} + \frac{m_2}{M_2} \right) \quad \text{or}$$

$$pV = (R^* T) \left(\frac{m_1}{M_1} + \frac{m_2}{M_2} \right) \quad (2.13a)$$

Dividing the above equation by the mass (m) of the mixture gives

$$p\alpha = (R^* T) \left\{ \frac{\frac{m_1}{M_1} + \frac{m_2}{M_2}}{m} \right\} \quad (2.14a)$$

Eq. (2.14a) shows that a mixture of ideal gases obeys a gas law which is of the same form as the ideal gas law for a single constituent.

Eq. (2.14a) can be rewritten in a way similar to (2.4),

$$p\alpha = \left(\frac{R^*}{\bar{M}} \right) T = \bar{R}T \quad (2.15)$$

where

$$\bar{R} = R^* / \bar{M} \quad \text{and} \quad \frac{1}{\bar{M}} = \frac{m_1/m}{M_1} + \frac{m_2/m}{M_2} \quad \text{or} \quad \bar{M} = \frac{1}{\frac{m_1/m}{M_1} + \frac{m_2/m}{M_2}}$$

The above argument may be extended to include a mixture of more than 2 gases (see reading assignment below – highlighted in light blue), i.e.

$$p\alpha = \left(\frac{R^*}{\bar{M}} \right) T = \bar{R}T \quad (2.15)$$

$$\frac{1}{\bar{M}} = \sum \left(\frac{m_i/m}{M_i} \right) \quad \text{or} \quad \bar{M} = 1 / \sum \left(\frac{m_i/m}{M_i} \right) \quad (2.16)$$

where \bar{R} and \bar{M} are called the **mean gas constant** and the **mean molecular weight**, respectively.

[Reading Assignment]

That is,

$$p = p_1 + p_2 + p_3 + \dots + p_n = \sum p_i, \quad (2.11)$$

where p is the total pressure of the mixture and p_i is the partial pressure of gas i .

In order to derive a gas law for a mixture of gases, let us consider individual gases. If each gas obeys separately the equation of state of an ideal gas, Eq. (2.2), then

$$p_i \alpha_i = R_i T = \left(\frac{R^*}{M_i} \right) T \quad \text{or} \quad p_i = \left(\frac{R^* T}{V} \right) \frac{m_i}{M_i}, \quad (2.12)$$

because $\alpha_i = V/m_i$. From Dalton's law, we can compute the total pressure of a mixture of gases,

$$p = \sum p_i = \left(\frac{R^* T}{V} \right) \sum \frac{m_i}{M_i} \quad \text{or} \quad pV = (R^* T) \sum \frac{m_i}{M_i} \quad (2.13)$$

Dividing Eq. (2.13) by the total mass $m = \sum m_i$ and recall $\alpha = V/\sum m_i$, we have

$$p\alpha = (R^* T) \sum \frac{(m_i/m)}{M_i} \quad (2.14)$$

Eq. (2.14) shows that a mixture of ideal gases obeys a gas law which is of the same form as the ideal gas law for a single constituent.

Eq. (2.14) can be rewritten in a way similar to (2.4),

$$p\alpha = \left(\frac{R^*}{\bar{M}} \right) T = \bar{R} T \quad (2.15)$$

where

$$\bar{R} = R^* / \bar{M} \quad \text{and}$$

$$\frac{1}{\bar{M}} = \sum \left(\frac{m_i/m}{M_i} \right) \quad \text{or} \quad \bar{M} = 1 / \sum \left(\frac{m_i/m}{M_i} \right) \quad (2.16)$$

are called the mean gas constant and the mean molecular weight, respectively.

Eq. (2.16) also tells us that the proper way to compute a mean molecular weight for a gas mixture is to take a mass-weighted harmonic mean.

Examples:

(1) Mean molecular weight of dry air

Composition of dry air

	by volume	by mass	$M(\text{kg/kmol})$
N ₂	78.09%	75.51%	28
O ₂	20.95%	23.14%	32
Ar	0.93%	1.30%	40
Other	0.03%	0.05%	---

Other gasses include CO₂, Ne, He, Kr, H₂, Xe, and O₃.

Since 99.95% of the atmosphere is made up of N₂+O₂+Ar by mass, the mass of the atmosphere can be well approximated by the mass of these three gases (*note: the composition of dry air may vary slightly, e.g., by increased emission of CO₂ into the atmosphere). In a moist atmosphere, the water vapor (H₂O) will make the major contribution to the variation of composition.

From Eq. (2.16), the mean molecular weight of the dry air may be estimated,

$$\begin{aligned}
 M_d &= 1/[(m_{\text{N}_2}/m)/M_{\text{N}_2}+(m_{\text{O}_2}/m)/M_{\text{O}_2}+(m_{\text{Ar}}/m)/M_{\text{Ar}}] \\
 &= 1/[0.7551/28+0.2314/32+0.0135/40] \\
 &= 28.97 \text{ kg kmol}^{-1}
 \end{aligned}$$

Thus, the [gas constant for dry air](#) may be derived by Eq. (2.16),

$$\begin{aligned}
 R_d &= R^*/M_d \\
 &= (8314.3 \text{ J kmol}^{-1} \text{ K}^{-1})/(28.97 \text{ kg kmol}^{-1}) \\
 &= 287.04 \text{ J kg}^{-1} \text{ K}^{-1}
 \end{aligned}$$

(2) Molecular weight of water vapor

$$M_v = 18 \text{ kg kmol}^{-1}$$

$$\begin{aligned}
 R_v &= R^*/M_v \\
 &= (8314.3 \text{ J kmol}^{-1} \text{ K}^{-1})/(18 \text{ kg kmol}^{-1}) \\
 &= 461 \text{ J kg}^{-1} \text{ K}^{-1}
 \end{aligned}$$

Thus

$$R_d/R_v = (R^*/M_d)/(R^*/M_v) = M_v/M_d = 18/28.97 = 0.622$$

This *magic number* 0.622 is very important in atmospheric thermodynamics. Notice that the [water vapor is lighter than the dry air](#) (per kmol).