Dalton's Law of Partial Pressures

John Dalton (1766 - 1844)

- In a gas mixture, each component gas behaves as if it alone occupied the entire volume.

- The pressure each component gas exerts in a mixture is its *partial pressure*, *p*.

☞ Dalton's Law of Partial Pressures:

> The total pressure of a gas mixture is the sum of the partial pressures; i.e.,

$$P_t = p_1 + p_2 + ... + p_n = \sum p_i$$

Partial Pressures and Mole Fractions

Consider a two-component gas mixture, composed of n_A moles of A(g) and n_B moles of B(g). The total pressure is

$$P_t = \frac{n_t RT}{V} = (n_A + n_B)\left(\frac{RT}{V}\right)$$

The partial pressure of A(g) is

$$p_A = n_A\left(\frac{RT}{V}\right) \Rightarrow \frac{p_A}{n_A} = \frac{RT}{V}$$

Substituting for RT/V in the previous expression for P_t

$$P_t = (n_A + n_B)\left(\frac{p_A}{n_A}\right)$$

Rearranging

$$p_A = \left(\frac{n_A}{n_A + n_B}\right) P_t$$

Partial Pressures and Mole Fractions - Continued

☞ We define the *mole fraction of A*, χ_A, as the number of moles of A in the mixture divided by the total number of moles (A plus B):

$$\chi_A \equiv \frac{n_A}{n_A + n_B}$$

Therefore,

$$p_A = \left(\frac{n_A}{n_A + n_B}\right) P_t = \chi_A P_t$$

or

$$\chi_A = p_A / P_t$$

Likewise,

$$p_B = \chi_B P_t \quad \text{or} \quad \chi_B = p_B / P_t$$

☞ In general, for a mixture of any number of non-reacting gases, for each component

$$p_i = \chi_i P_t \quad \text{or} \quad \chi_i = p_i / P_t$$

Special Relationships for a Two-Component Mixture

- For any mixture, the sum of the mole fractions for all components must add to 1.

$$\chi_1 + \chi_2 + \ldots + \chi_n = \sum \chi_i = 1$$

For a two-component mixture, then

$$\chi_A + \chi_B = 1$$

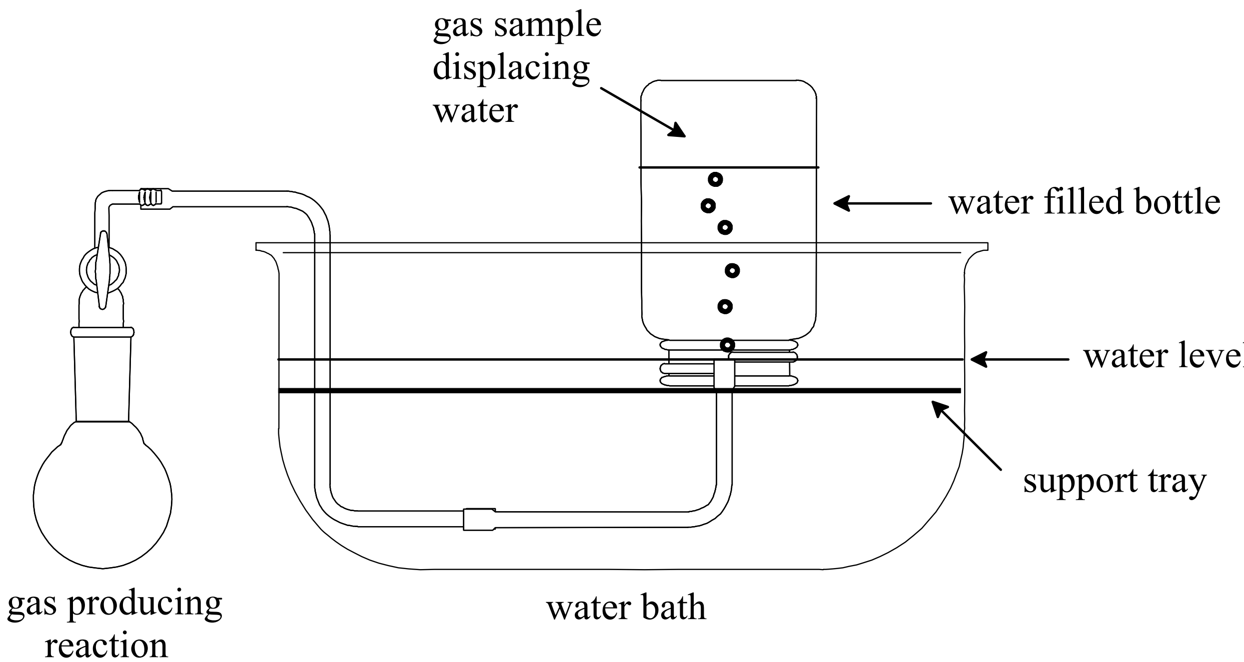
Substituting into the previous expressions for p_A and p_B, we can write

$$p_A = (1 - \chi_B)P_t$$

and

$$p_B = (1 - \chi_A)P_t$$

Collecting a Gas Sample by Water Displacement



Vapor Pressure of Water

T (ºC)	*p* (atm)	*p* (torr)	T (ºC)	*p* (atm)	*p* (torr)
10	0.0121	9.2	27	0.0352	26.7
11	0.0130	9.8	28	0.0373	28.3
12	0.0138	10.5	29	0.0395	30.0
13	0.0148	11.2	30	0.0419	31.8
14	0.0158	12.0	31	0.0443	33.7
15	0.0168	12.8	32	0.0470	35.7
16	0.0179	13.6	33	0.0496	37.7
17	0.0191	14.5	34	0.0525	39.9
18	0.0204	15.5	35	0.0555	42.2
19	0.0217	16.5	40	0.0728	55.3
20	0.0231	17.5	45	0.0946	71.9
21	0.0245	18.7	50	0.122	92.5
22	0.0261	19.8	60	0.197	149.4
23	0.0277	21.1	70	0.308	233.7
24	0.0294	22.4	80	0.467	355.1
25	0.0313	23.8	90	0.692	525.8
26	0.0332	25.2	100	1.000	760.0

Graham's Law of Effusion

Thomas Graham (1805 - 1869)

- *Effusion* is the escape of a gas from a container through an tiny opening or *orifice*.

☞ Graham's Law of Effusion: Under constant temperature and pressure, the rate of effusion of a gas is inversely proportional to the square root of its molecular weight (molar mass).

$$r = \frac{k}{\sqrt{M}}$$

- k is a constant for the apparatus under certain conditions of temperature and pressure.

Comparing Two Effusing Gases

Consider two gases at the same temperature and pressure effusing from containers with the same size orifice.

From Kinetic Molecular Theory, if *T* is constant, both gases have the same mean kinetic energy

$$K_A = K_B \quad \Rightarrow \quad \tfrac{1}{2} m_A v_A^{\,2} = \tfrac{1}{2} m_B v_B^{\,2} \;\Rightarrow\; m_A v_A^{\,2} = m_B v_B^{\,2}$$

where v is the root mean squared velocity (v_{rms}), and m is the mass of an individual molecule.

Rearranging,

$$\frac{v_A^2}{v_B^2} = \frac{m_B}{m_A} \quad \Rightarrow \quad \frac{v_A}{v_B} = \sqrt{\frac{m_B}{m_A}}$$

The rate of effusion is proportional to the rate at which the molecules strike the orifice, which in turn is proportional to the molecular velocity, so

$$\frac{r_A}{r_B} = \sqrt{\frac{m_B}{m_A}}$$

Comparing Two Effusing Gases - Continued

The ratio m_A/m_B is the same as M_A/M_B, so

$$\frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}}$$

Graham's Law and Gas Density

Moles times molecular weight is mass in grams, so density is

$$d = \frac{Mn}{V} = M\left(\frac{n}{V}\right) = \left(\frac{\mathrm{g}}{\mathrm{mol}}\right)\left(\frac{\mathrm{mol}}{\mathrm{L}}\right) = \frac{\mathrm{g}}{\mathrm{L}}$$

Therefore,

$$d_A = M_A\left(\frac{n_A}{V}\right) \qquad d_B = M_B\left(\frac{n_B}{V}\right)$$

At constant temperature and pressure all gases have the same number of moles per liter:

$$\frac{n}{V} = \frac{P}{RT} = \text{constant}$$

Thus, $n_A/V = n_B/V$, and it follows that $M_B/M_A = d_B/d_A$.

Substituting into the conventional Graham's Law expression

$$\frac{r_A}{r_B} = \sqrt{\frac{d_B}{d_A}}$$