Annex B
The Dalton's Law of Partial Pressures

In 1801 the English chemist John Dalton enunciated a physical law that took his name:

The partial pressure exerted by a gas in a mixture of non-reactive gases is the pressure the gas would exert if it alone occupied the whole container. The total pressure in the container is the sum of all partial pressures of each gas (Figure 1).

This law is a consequence of the Ideal Gas Law, as it will be demonstrated next.

Gas A		Gas B		Mixture of A + B
p1 = 100 mmHg	+	p2 = 300 mmHg	=	p = 400 mmHg
V = 2 liters		V = 2 liters		V = 2 liters
p1 V = (m1 / M1) R T		p2 V = (m2 / M2) R T		p V = (m / M) R T

Figure 1
Illustration of Dalton's Law of Partial Pressures

Demonstration of the Dalton's Law

In the volume V of a gas mixture, suppose that (by some means) all molecules of gas A are extracted, leaving only N_2 molecules of gas B. In this situation:

$$p_2\, V = N_2\, k\, T \qquad (1)$$

where k is the Boltzmann constant (Annex A). Similarly, if all the molecules of gas B are extracted, leaving only N1 molecules of gas A:

$$p_1\, V = N_1\, k\, T \qquad (2)$$

When the two gases are mixed in volume V, with $N = N_1 + N_2$

$$p\, V = (N_1 + N_2)\, k\, T \qquad (3)$$

Adding expressions (1) and (2) and equating to (3):

$$\boxed{p_1 + p_2 = p}$$

which is the mathematical expression of Dalton's Law.

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On the other hand, if the molecules of gases A and B are <u>separated</u> (by any means) within the volume V, gas A will occupy a volume V_1 and gas B a volume V_2 given by:

$$V_1 = \frac{N_1 kT}{p} \qquad V_2 = \frac{N_2 kT}{p} \tag{4}$$

Then $V_1 + V_2 = V$.

The <u>relative amounts</u> **a** and **b** of gases A and B in the mixture are:

$$\begin{aligned} a &= \frac{V_1}{V_1 + V_2} = \frac{N_1}{N_1 + N_2} \\ b &= \frac{V_2}{V_1 + V_2} = \frac{N_2}{N_1 + N_2} \\ a + b &= 1 \end{aligned} \tag{5}$$

Dividing (2) by (3), (1) by (3), and using (5):

$$\boxed{\begin{aligned} p_1 &= ap \\ p_2 &= bp \end{aligned}}$$

an easy way to compute the partial pressures.

Finally, the molar mass M <u>of the mixture</u> is the weighted average of M_1 and M_2:

$$\boxed{M = aM_1 + bM_2}$$

Demonstration:

$$M = aM_1 + bM_2 = a\frac{m_1 RT}{p_1 V} + b\frac{m_2 RT}{p_2 V} = \frac{RT}{V}\left(\frac{am_1}{ap} + \frac{bm_2}{bp}\right) =$$

$$= \frac{RT}{pV}(m_1 + m_2) = m\frac{RT}{pV} = M$$

Example

Moist air at 20ºC and 1.0 atmosphere contains water vapor with a density of 10 milli-grams/liter (100 drops/liter). Determine all variables found in the Ideal Gas and Dalton's Laws.

The table below shows how values must be computed:

Variable	Value	Meaning
R	0.08207 atm liters / mol / ºK	universal gas constant
T	20ºC + 273ºC = 293 ºK	temperature of mixture
M_1	18 g/mol	molar mass of water
M_2	29 g/mol	molar mass of dry air
V	1 liter	volume of mixture
m_1	10 mg	mass of water vapor
p	1 atm	atmospheric pressure (total pressure of gas mixture forming the atmosphere)
n_1	m_1/M_1 = 0.01 / 18= 0.000556 moles	number of moles of water vapor
V_1	n_1 R T / p = 0.000556 x 0.08207 x 293 / 1 = 13.4 mL	volume occupied by the water vapor in the mixture
V_2	V - V_1 = 1 - 0.0137 = 0.9866 liters	volume occupied by dry air in the mixture
n_2	p V_2 / R T = 1 x 0.9866 / 0.08207 / 293 = 0.041 moles	number of moles of dry air
n	n_1 + n_2= 0.04156 moles	number of moles of mixture
m_2	n_2 M_2 = 0.041 x 29 = 1.19 grams	mass of dry air
m	m_1 + m_2 = 0.01 + 1.19 = 1.20 grams	mass of the mixture
a	V_1 / V = 0.0134 / 1 = 1.34%	% vapor in the mixture
b	V_2 / V = 0.9866 / 1 = 98.66%	% dry air in the mixture
M	a M_1 + b M_2 = 0.0134 x 18 + 0.9866 x 29 = 28.85 g/mol	molecular mass of mixture
p1	a p = 0.0134 x 1 = 0.0134 atm=10.2 mmHg	partial pressure of water vapor in the mixture
p2	b p = 0.9866 x 1 = 0.9866 atm = 749.8 mmHg	partial pressure of dry air in the mixture

Variables of the Psychrometric Chart:

Absolute Humidity HR = 1000 * m_1 / m_2 = 8.41 g / kg

Relative Humidity RH = p1 / p_S(20ºC) = 10.2 mmHg / 17.4 mmHg = 58.2 %

Specific Volume SV = V / m_2 = 1 liter / 1.19 g = 0.841 m^3 / kg

Historical note: John Dalton (1766-1844) was the first one to provide a scientific description of color blindness, a condition from which he suffered. Now-a-days, this deficiency is called "Daltonism."