"Dalton's Law of Partial Pressures": Facts and Myth

Facts:

- J. Dalton (around 1801) found experimentally that, for a mixture of N gaseous species of amounts n_i in a container of a given T and V, if he placed each species individually in the container (at the same T and V) and measured the pressure in the container in each case, P_i^*, then a reasonable approximation for the pressure of the mixture was given by

$$P(V, T, n_1, n_2, \ldots, n_N) = \sum_{i=1}^{N} P_i^*(V, T, n_i) \tag{1}$$

  $P_i^*(V, T)$, the pressure of n_i moles of pure component i at a given (V, T), is called the *pure component pressure* of that component. The approximation of equation (1) is called *Dalton's Law of Pure-Component Pressures* or *Dalton's Law of Additive Pressures.*

- Confusion arises in most introductory chemistry texts, since the *pure-component pressure* is distinct from the *partial pressure*, p_i, of component i in a mixture. The latter is *defined* by

$$p_i = y_i P$$

  where P is the (total) pressure of the mixture.

- Note further that the partial pressures always sum to the total pressure, due to above definition, since

$$\sum_{i=1}^{n} p_i = \sum_{i=1}^{n} y_i P = P \sum_{i=1}^{n} y_i = P \tag{2}$$

  i.e.

$$\sum_{i=1}^{n} p_i = P \tag{3}$$

- Equation (1) is an *approximation*; equation (3) results from the *definition* of the partial pressure.

Myth:

- There is much confusion in textbooks concerning the distinction between equations (1) and (3). The latter is often called *Dalton's Law of Partial Pressures.* The use of this term is confusing at best, since (3) is simply a consequence of the definition of the partial pressure. At worst, it is misleading, since very rarely do students ever learn to appreciate the distinction.

  A sampling of the confusion is contained in the following references (all of which consider only mixtures of ideal gases):

  G. W. Castellan, *Physical Chemistry, 3rd ed.*, Benjamin/Cummings, 1983, p. 19

  R. A. Alberty and R. J. Silbey, *Physical Chemistry, 1st ed.*, Wiley, 1992, p. 10.

I. M. Klotz and R. M. Rosenberg, *Chemical Thermodynamics, Basic Theory and Methods,
5th ed.*, Wiley-Interscience, 1994, p. 266.

R. E. Sonntag and G. J. van Wylen, *Introduction to Thermodynamics, Classical and Statistical, 5th ed.*, J. Wiley & Sons, 1998, p. 440 (they even state "It should be stressed that the
term partial pressure is relevant only for ideal gases.")

- The reason for the confusion between equations (1) and (3) can be traced to calculations
  that one typically performs in first-year chemistry related to the (essentially exclusive) use of
  the ideal-gas equation of state. To see this, consider a mixture of ideal gases, whose equation
  of state is given by

$$PV = nRT$$

Multiplying this equation by the mole fraction of any component, y_i, gives

$$(y_i P)V = (y_i n)RT \tag{4}$$

or equivalently,

$$p_i = \frac{n_i RT}{V} \tag{5}$$

where p_i is the partial pressure and n_i is the molar amount of n_i in the mixture. Now
consider placing n_i moles of ideal-gas species i in a container of volume V at temperature
T. Its (pure-component) pressure is given by the usual ideal-gas formula

$$P_i^* = \frac{n_i RT}{V} \tag{6}$$

Thus, for a mixture of ideal gases, the partial pressure and the pure-component pressures
are equal. A consequence of this is the fact that *both* the partial pressures *and* the pure-component pressures sum to the total pressure for a mixture of ideal gases. In this case, the
term "Dalton's Law of Partial Pressures" is often used to denote *either* of (3) or (1). These
are *equivalent statements* for an ideal gas mixture. However, it serves no purpose to promote
this simple result that holds only for ideal gases to the status of a "law".

Summary:

- The term "Dalton's Law of Pure-Component Pressures" is best reserved for equation(1).
  The term "Dalton's Law of Partial Pressures" should not be used at all, since the partial
  pressures add to the total pressure by definition.

- Equation (1) is an *approximation* for a mixture of gases (fluids in general). If the gases
  obey the ideal-gas equation of state, then there is really no point in using either term. If
  the ideal gas equation of state is the only equation of state considered (typically the case in
  first-year chemistry classes), use of the term "Dalton's Law of Partial Pressures" can create
  an incorrect impression in the minds of students, and confusion between equations (3) (a
  definition) and (1) (an approximation).

- Dalton's Law of Pure-Component Pressures can be used as an approximation to calculate the PVT properties of mixtures. In order to implement it, one must have available an equation of state (EOS) for the pure components. Any such EOS may be used in principle, including generalized compressibility charts. Of course, the numerical results will differ, depending on the EOS used.

- A related approximation in the spirit of Dalton's Law is Amagat's Law of Additive Volumes. In this case, the approximation is that

$$V(T, P, n_1, n_2, \ldots, n_N) = \sum_{i=1}^{N} V_i^*(T, P, n_i) \tag{7}$$

where V_i^* is the *pure-component volume* of n_i moles of species i at the T, P of the mixture. As for Dalton's Law, this approximation is obeyed exactly by a mixture of ideal gases.

- In practise, Amagat's Law (which is equivalent to the approximation of ideal mixing), is generally more quantitatively accurate than Dalton's Law. In fact, the former can even be used reasonably for liquids. If it is assumed to hold universally for the fluid, then this is equivalent to the *Lewis-Randall fugacity rule* for the nonideal part of the chemical potential.