Dalton's Law vs. Amagat's Law for the Mixture of Real Gases

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We are familiar with English scientist John Dalton who proposed the existence of atoms. He also found the law of partial pressure from his experiment on the mixture of gases. Actually Dalton performed the above gas experiment in order to suggest the atomic theory of matter.

In modern terminology a fundamental property of gas mixtures discovered by Dalton (1801) is: the pressure of a mixture of gases is equal to the sum of the pressures each of its components would exert if alone in the volume of the mixture at the same temperature. Thus Dalton's law implies that each component acts independently in its contribution to the total pressure, or, more picturesquely, that "every gas is a vacuum to every other gas." Dalton's law can be stated more concisely in terms of partial pressure. Thus Dalton's law can be written

$$P = \sum_i P_i \tag{1}$$

A system obeying Dalton's law exactly is known as an ideal mixture, irrespective of whether its components individually behave as ideal gases.

An alternative approach to the properties of gaseous mixtures leads to Amagat's law (1880): the volume of a mixture of gases is the sum of the volumes of its components, each at the pressure and temperature of the mixture. In symbols,

$$V = \sum_i V_i \tag{2}$$

where the quantities V_i are called partial volumes.

The concept of partial volumes, in a mixture already constituted, is purely mathematical and has no physical

significance. Partial pressures, on the other hand, can in certain circumstances, be observed directly. If the vessel containing a gas mixture were connected to a manometer through a membrane permeable to only one of the components, the manometer would read the partial pressure of that component. Thus a partial pressure measurement could be realized in a mixture containing H_2 by using palladium foil as the membrane. Fig. 1 is a demonstration of the partial pressure of H_2.

Our attention was originally drawn to this subject when we noticed that some of our colleagues who teach general chemistry seem to have little understanding of the approximation behind the gas laws and of its relationship to the virial coefficients.

Real gases show deviations from the perfect gas law because molecules interact with each other. Thus real gases are expressed more precisely as the following:

$$PV = nRTz_{mix}(P,T) \tag{3}$$

where $z_{mix}(P, T)$ is called the compressibility factor.

Also Dalton's and Amagat's laws for gas mixtures can be expressed more precisely in terms of the compressibility factor.

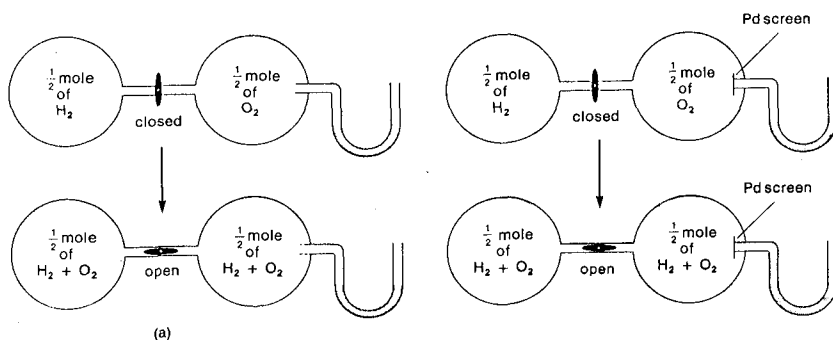According to Dalton's law the partial pressure P_i is by

FIGURE 1. Demonstration of the partial pressure of H_2, using palladium foil, which is permeable only to H_2. The upper assemblage in both panels (a) and (b) shows the initial state of the system in which the stopcock is closed. The presence or absence of the Pd foil does not affect the state at this point. The lower assemblage in panel (a) shows the state of the system after the stopcock is opened. The lower assemblage in panel (b) shows the state of a system with a Pd foil, after the stopcock is opened.

definition the pressure n_i moles of component i would exert if alone at the volume and temperature of the mixture. If the components are treated as real gases, then in analogy with (3)

$$P_iV = n_iRTz_i(P_i,T) \tag{4}$$

where $z_i(P_i, T)$ is the compressibility factor for component i evaluated at its partial pressure P_i. Summing (4) over i and using (1), we obtain

$$PV = \sum_i n_iRTz_i(P_i,T) \tag{5}$$

Comparing (5) with (3), we find that the compressibility factor for a mixture can be expressed

$$nz_{mix}(P,T) = \sum_i n_iz_i(P_i,T) \tag{6}$$

Or using the definition of mole fraction

$$x_i = \frac{n_i}{n} \tag{7}$$

$$z_{mix}(P,T) = \sum_i x_iz_i(P_i,T) \quad \text{(Dalton)} \tag{8}$$

Thus Dalton's law implies that the compressibility factor for a mixture is approximated by the weighted average of the compressibility factors of the components, each evaluated at the appropriate partial pressure.

Amagat's law can be reexpressed in analogous fashion. According to this principle, the partial volume V_i is , by definition, the volume n_i moles of component i would occupy at the pressure and temperature of the mixture. Thus in analogy with (3)

$$PV_i = n_iRTz_i(P,T) \tag{9}$$

Summing (9) over i and using (2),

$$PV = \sum_i n_iRTz_i(P,T) \tag{10}$$

Thus the amagat compressibility factor for a mixture is given by

$$z_{mix}(P,T) = \sum_i x_iz_i(P,T) \quad \text{(Amagat)} \tag{11}$$

Comparing (11) with (8), we are able to contrast Dalton's and

Amagat's laws from a more fundamental point of view. Both laws for ideal mixtures are based on an additive approximation for $z_{mix}(P, T)$. According to Dalton's law, the component compressibility factors are evaluated at the respective partial pressures - hence $z_i(P_i, T)$ - whereas, according to Amagat's law, the component compressibility factors are evaluated at the total pressure of the mixture - hence $z_i(P, T)$.

To illustrate the laws of gas mixtures, consider the system $3/4\ H_2 + 1/4\ N_2$ at 0°C. Referring to Fig. 2, the curve labeled
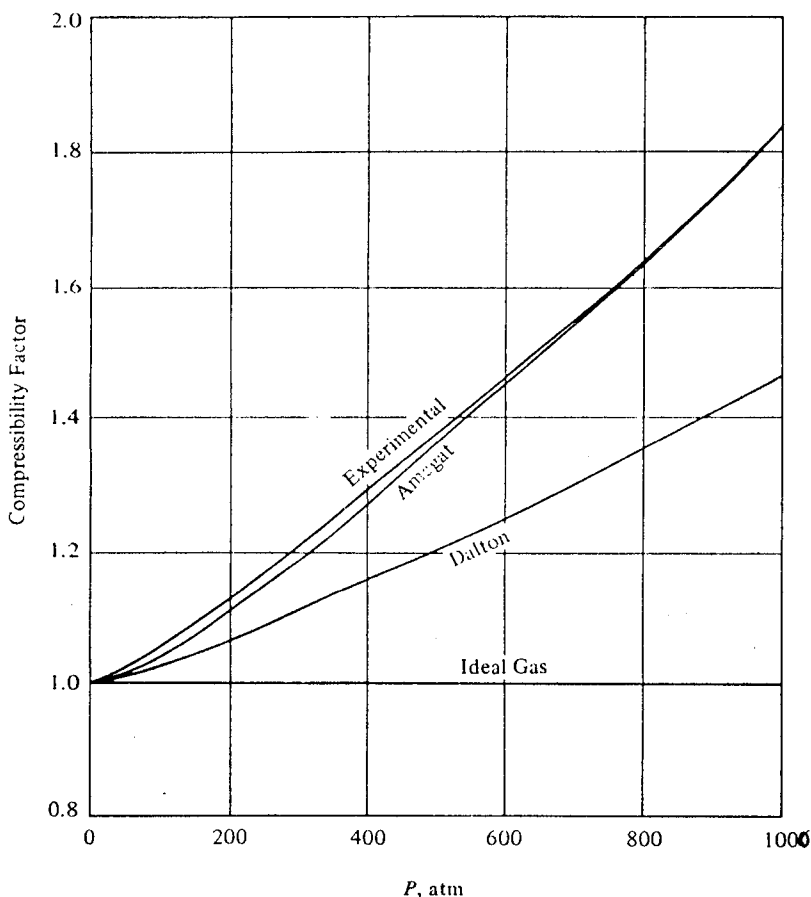

FIGURE 2. Experimental and Calculated Compressibility Factors for the System $3/4\ H_2 + 1/4\ N_2$ at 0°C. The experimental isotherm is based on the data of Bartlett, Cupples, and Tremearne, 1928, *J. Am. Chem. Soc.*, 50, 1275.

"experimental" gives the measured compressibility factor isotherm for the mixture,

$$z_{mix}(P,T) = \frac{PV}{nRT} \tag{12}$$

At 1000 atm, z_{mix}=1.8029. The ideal gas law applied to the gas mixture implies $z_{mix}(P,T)$=1. This is seen to be inadequate except at the lowest pressures.

Dalton's law is evidently an adequate approximation up to about 100 atm but it fails thereafter. Amagat's law, on the other hand, provides an excellent approximation for pressures even exceeding 1000 atm.

Both Dalton's and Amagat's law are inexact because they neglect the perturbing effect of one component in a mixture on the state variable of the other components.

The general approach to representing the PVT behavior of real gases starts with the definition of the compressibility factor:

$$z = \frac{PV_m}{RT} \tag{13}$$

This quantity is clearly equal to one for an ideal gas and, for real gases, will approach one as the pressure and concentration approach zero. In such a case we might represent z as a power series in the molar concentration n/V=$1/V_m$:

$$z = 1 + B\left(\frac{1}{V_m}\right) + C\left(\frac{1}{V_m}\right)^2 + D\left(\frac{1}{V_m}\right)^3 + E\left(\frac{1}{V_m}\right)^4 + K \tag{14}$$

The coefficients of this expansion are functions of T only and are called the virial coefficients.

The significance of the virial series is primarily theoretical. The second virial coefficient, $B(T)$, can be calculated from the forces between molecules interacting two at a time.

The statistical theory of intermolecular interactions which led to the virial equation can also be applied to mixtures. For a two-component mixture with molecules of types 1 and 2, the calculation of the second virial coefficient must consider three types of pairwise interactions: 1-1, 1-2 and 2-2. The result is:

$$B = x_1^2 B_1 + x_2^2 B_2 + 2x_1 x_2 B_{12} \tag{15}$$

where B_1 and B_2 are the second virial coefficients of the pure

gases, and B_{12} is the second virial coefficient calculated with the potential function U_{12} for interactions between the unlike molecules.

We can show that Dalton's law corresponds to assuming $B_{12}=0$. From the virial equation neglecting all but the B term, we get for each gas (alone in volume V):

$$P_1 V = n_1 RT + \frac{n_1^2 RTB_1}{V} \tag{16}$$

$$P_2 V = n_2 RT + \frac{n_2^2 RTB_2}{V} \tag{17}$$

With $P=P_1+P_2$:

$$PV = (n_1 + n_2)RT + \frac{RT}{V}(n_1^2 B_1 + n_2^2 B_2) \tag{18}$$

Dividing by $(n_1 + n_2)$ and defining $V_m = V/(n_1+n_2)$:

$$\frac{PV_m}{RT} = 1 + (x_1^2 B_1 + x_2^2 B_2)\frac{1}{V_m} \tag{19}$$

Comparing (19) with (14) and (15) shows that this is the result if $B_{12} = 0$; in effect, Dalton's law ignores interactions of unlike molecules.

We also show that Amagat's law corresponds to assuming that the forces between unlike molecules are similar to those between like molecules, and that the cross-virial coefficient is the mean:

$$B_{12} = \frac{B_1 + B_2}{2} \tag{20}$$

To prove this we start with (14) (keeping B term and neglecting higher-order terms). The volumes of the pure gases are:

$$V_1 = \frac{n_1 RT}{P} + n_1 B_1 \tag{21}$$

$$V_2 = \frac{n_2 RT}{P} + n_2 B_2 \tag{22}$$

From (2), the volume of the gases together is:

$$V = V_1 + V_2 \frac{(n_1 + n_2)RT}{P} + n_1 B_1 + n_2 B_2 \tag{23}$$

$$V_m = \frac{RT}{P} + (x_1 B_1 + x_2 B_2) \tag{24}$$

The virial coefficient of the mixture is therefore:

$$B = x_1 B_1 + x_2 B_2 \tag{25}$$

If, in (15), we use $B_{12}=(B_1+B_2)/2$, we get:

$$B = x_1^2 B_1 + x_2^2 B_2 + x_1 x_2 B_1 + x_1 x_2 B_2$$
$$= x_1(x_1 + x_2)B_1 + x_2(x_1 + x_2)B_2 \tag{26}$$

Since $x_1 + x_2 = 1$, this is the same result as Amagat's law.

In the following table, the second virial coefficient considering three kinds of pairwise interactions in the binary mixture are summarized for each gas law.

Gas Law \\ Virial Coeff.	B_1	B_2	B_{12}
Ideal Gas Law	0	0	0
Dalton's Law	$B_1 \neq 0$	$B_2 \neq 0$	0
Amagat's Law	$B_1 \neq 0$	$B_2 \neq 0$	$(B_1+B_2)/2$

The significance of the preceding derivation is that, in a mixture of gases (black and white), Dalton's law calculates the properties of a gas (black) assuming the other gas (white) is not there, whereas Amagat's law calculates the properties of the black molecules assuming that the white molecules are there and interact with the black just as do other black molecules. Put another way, the ideal gas law assumes that molecules are blind, they "see" no other molecules; Dalton's law assumes that the molecules are selectively blind, they see only molecules of their own "color"; Amagat's law assumes that the molecules are colorblind, they "see" all molecules but think they are the same color.

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