

2.14: Gas Mixtures - Dalton's Law of Partial Pressures

Thus far, our discussion of the properties of a gas has implicitly assumed that the gas is pure. We turn our attention now to mixtures of gases—gas samples that contain molecules of more than one compound. Mixtures of gases are common, and it is important to understand their behavior in terms of the properties of the individual gases that make it up. The ideal-gas laws we have for mixtures are approximations. Fortunately, these approximations are often very good. When we think about it, this is not surprising. After all, the distinguishing feature of a gas is that its molecules do not interact with one another very much. Even if the gas is composed of molecules of different kinds, the unimportance of molecule—molecule interactions means that the properties of one kind of molecules should be nearly independent of the properties of the other kinds.

Consider a sample of gas that contains a fixed number of moles of each of two or more compounds. This sample has a pressure, a volume, a temperature, and a specified composition. Evidently, the challenge here is to describe the pressure, volume, and temperature of the mixture in terms of measurable properties of the component compounds.

There is no ambiguity about what we mean by the pressure, volume, and temperature of the mixture; we can measure these properties without difficulty. Given the nature of temperature, it is both reasonable and unambiguous to say that the temperature of the sample and the temperature of its components are the same. However, we cannot measure the pressure or volume of an individual component in the mixture. If we hope to describe the properties of the mixture in terms of properties of the components, we must first define some related quantities that we can measure. The concepts of a component partial pressure and a component partial volume meet this need.

We define the **partial pressure** of a component of a gas mixture as the pressure exerted by the same number of moles of the pure component when present in the volume occupied by the mixture, $V_{mixture}$, at the temperature of the mixture. In a mixture of n_A moles of component A , n_B moles of component B , etc., it is customary to designate the partial pressure of component A as P_A . It is important to appreciate that the partial pressure of a real gas can only be determined by experiment.

We define the **partial volume** of a component of a gas mixture as the volume occupied by the same number of moles of the pure component when the pressure is the same as the pressure of the mixture, $P_{mixture}$, at the temperature of the mixture. In a mixture of components A , B , etc., it is customary to designate the partial volume of component A as V_A . The partial volume of a real gas can only be determined by experiment.

Dalton's law of partial pressures asserts that the pressure of a mixture is equal to the sum of the partial pressures of its components. That is, for a mixture of components A , B , C , etc., the pressure of the mixture is

$$P_{mixture} = P_A + P_B + P_C + \dots \quad (2.14.1)$$

Under conditions in which the ideal gas law is a good approximation to the behavior of the individual components, Dalton's law is usually a good approximation to the behavior of real gas mixtures. For mixtures of ideal gases, it is exact. To see this, we recognize that, for an ideal gas, the definition of partial pressure becomes

$$P_A = \frac{n_A RT}{V_{mixture}}$$

The ideal-gas mixture contains $n_{mixture} = n_A + n_B + n_C + \dots$ moles, so that

$$\begin{aligned} P_{mixture} &= \frac{n_{mixture} RT}{V_{mixture}} \\ &= \frac{(n_A + n_B + n_C + \dots) RT}{V_{mixture}} \\ &= \frac{n_A RT}{V_{mixture}} + \frac{n_B RT}{V_{mixture}} + \frac{n_C RT}{V_{mixture}} + \dots \\ &= P_A + P_B + P_C + \dots \end{aligned}$$

Applied to the mixture, the ideal-gas equation yields Dalton's law (Equation 2.14.1). When x_A is the mole fraction of A in a mixture of ideal gases,

$$P_A = x_A P_{mixture}.$$

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