

The chemist's toolkit 3 The perfect gas

Many of the basic equations of chemical thermodynamics are developed by using the equation of state of a perfect gas. That starting point is used even if the ultimate aim is the development of expressions for biologically significant species in the environment typical of cells. That is because it gives expressions that can be adapted to take into account the interactions that take place in real systems far removed from being gas-like.

An **equation of state** is an expression that expresses one variable (typically the pressure, p) in terms of other variables of the system (such as the amount of substance present, n ; the volume, V , occupied by the sample, and the absolute temperature, T). All equations of state have the form $p = f(n, V, T)$. The experiments of Boyle, Charles, and others, principally in the 17th century, established the approximate relation

$$p = \frac{nRT}{V}$$

where R is a constant the same for all gases, and known as the **gas constant**. Its modern value is $R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$. This equation of state is commonly written $pV = nRT$.

Although approximate, this equation of state is found to be obeyed more exactly as the pressure of the gas is reduced, and is exact in the limit of zero pressure. It is therefore an example of

a **limiting law**, a law that becomes exact in some limit (in this case, as $p \rightarrow 0$). A hypothetical gas that obeys the equation of state at all pressures is called a **perfect gas** (or an *ideal gas*). The perfect gas equation of state is an excellent approximation to the equations of state of real gases under all normal conditions, and is used throughout thermodynamics for the starting point for the development of equations for all kinds of systems, including the aqueous environment of cells.

The total pressure of a mixture of perfect gases is the sum of each of their **partial pressure**, p_p , where

$$p_j = \frac{n_j RT}{V}, \quad p = p_A + p_B + \dots$$

This conclusion expresses Dalton's law, that the total pressure of a gas is the sum of the pressures that each component of the mixture would exert if it occupied the container alone. Partial pressures are also defined for real gases as

$$p_j = x_j p, \quad x_j = \frac{n_j}{n}, \quad n = n_A + n_B + \dots$$

Although it remains true that the sum of the partial pressures is equal to the total pressure, the partial pressure is no longer equal to the pressure the component would exert if it were alone in the container.