

6.1: The Ideal Gas Equation

In 1660, the Honorable Robert Boyle, Father of Chemistry and seventh son of the Earl of Cork, and one of the founders of the Royal Society of London, conducted certain *Experiments Physico-Mechanical Touching the Spring of the Air*. He held a quantity of air in the closed arm of a J-shaped glass tube by means of a column of mercury and he measured the volume of the air as it was subjected to greater and greater pressures. As a result of these experiments he established what is now known as *Boyle's Law*:

The pressure of a fixed mass of gas held at constant temperature (i.e. in an isothermal process) is inversely proportional to its volume.

That is,

$$PV = \text{constant.} \quad (6.1.1)$$

Later experiments showed that the volume of a fixed mass of gas held at constant pressure increases linearly with temperature. In particular, most gases have about the same volume coefficient of expansion. At 0°C this is about $0.00366 \text{ } ^\circ\text{C}^{-1}$ or $1/273 \text{ } ^\circ\text{C}^{-1}$.

If you extrapolate the volume of a fixed mass of gas held at constant pressure to lower and lower temperatures, the extrapolated volume would fall to zero at $-273 \text{ } ^\circ\text{C}$. This is not directly the basis of our belief that no temperatures are possible below $-273 \text{ } ^\circ\text{C}$. For one thing, a real gas would liquefy long before that temperature is reached. Nevertheless, for reasons that will be discussed in a much later chapter, we do believe that this is the absolute zero of temperature. In any case:

The volume of a fixed mass of gas held at constant pressure (i.e. in an isobaric process) is directly proportional to its Kelvin temperature.

Lastly,

The pressure of a fixed mass of gas held at constant volume (i.e. in an isochoric process) is directly proportional to its Kelvin temperature.

If P , V and T are all allowed to vary, these three laws become

$$PV/T = \text{constant} \quad (6.1.2)$$

The value of the constant depends on how much gas there is; in particular, it is proportional to how many moles (hence how many molecules) of gas there are. That is

$$PV/T = RN, \quad (6.1.3)$$

where N is the number of moles and R is a proportionality constant, which is found to be about the same for most gases.

Of course real gases behave only approximately as described, and only provided experiments are performed over modest ranges of temperature, pressure and volume, and provided the gas is well above the temperature at which it will liquefy. Nevertheless, provided these conditions are satisfied, most gases do conform quite well to equation 6.1.3 with about the same proportionality constant for each.

A gas that obeys the equation

$$PV = NRT \quad (6.1.4)$$

exactly is called an *Ideal Gas*, and equation 6.1.4 is called the *Equation of State for an Ideal Gas*. In this equation, V is the total volume of the gas, N is the number of moles and R is the Universal Gas Constant. The equation can also be written

$$PV = RT. \quad (6.1.5)$$

In this case, V is the *molar volume*. Some authors use different symbols (such as V , v and V_m) for total, specific and molar volume. This is probably a good idea, and it is at some risk that I am not going to do this, and I am going to hope that the context will make it clear which volume I am referring to when I use the simple symbol V in any particular situation. Note that, while total volume is an *extensive* quantity, specific and molar volumes are *intensive*.

It is not impossible to go wrong by a factor of 10^3 when using equation 6.1.5. If you are using CGS units, P will be expressed in dynes per square cm, V is the volume of a mole (i.e. the volume occupied by 6.0221×10^{23} molecules), and the value of the universal gas constant is $.83145 \times 10^7 \text{ erg mole}^{-1} \text{ K}^{-1}$. If you are using SI units, P will be expressed in pascal (N m^{-2}), V will be the

volume of a kilomole (i.e. the volume occupied by 6.0221×10^{26} molecules), and the value of the universal gas constant is $8.3145 \times 10^3 \text{ J kilomole}^{-1} \text{ K}^{-1}$. If you wish to express pressure in Torr, atm. or bars, and energy in calories, you're on your own.

You can write equation 6.1.4 (with V = total volume) as $P = \frac{N N_A}{V} \frac{RT}{N_A}$ where N_A is Avogadro's number, which is 6.0221×10^{23} molecules per mole, or 6.0221×10^{26} molecules per kilomole. The first term on the right hand side is the total number of molecules divided by the volume; that is, it is the number of molecules per unit volume, n . In the second term, R/N_A is *Boltzmann's constant*, $k = 1.3807 \times 10^{-23} \text{ J K}^{-1}$. Hence the equation of state for an ideal gas can be written

$$P = nkT. \quad (6.1.6)$$

Divide both sides of equation 6.1.5 by the molar mass ("molecular weight") μ . The density ρ of a sample of gas is equal to the molar mass divided by the molar volume, and hence the equation of state for an ideal gas can also be written

$$P = \frac{\rho RT}{\mu}. \quad (6.1.7)$$

In summary, equations 6.1.4, 6.1.5, 6.1.6 and 6.1.7 are all commonly-seen equivalent forms of the equation of state for an ideal gas. From this point on I shall use V to mean the *molar volume*, unless stated otherwise, so that I shall use equation 6.1.5 rather than 6.1.4 for the equation of state for an ideal gas. Note that the molar volume (unlike the total volume) is an *intensive* state variable.

In September 2007, the values given for the above-mentioned physical constants on the Website of the National Institute of Science and Technology (<http://physics.nist.gov/cuu/index.html>) were:

Molar Gas Constant $R = 8314.472 \text{ (15) J kmole}^{-1} \text{ K}^{-1}$.

Avogadro Constant $N_A = 6.022 \ 141 \ 79 \text{ (30)} \times 10^{26} \text{ particles kmole}^{-1}$.

Boltzmann Constant $k = 1.380 \ 6504 \text{ (24)} \times 10^{-23} \text{ J K}^{-1} \text{ per particle}$.

The number in parentheses is the standard uncertainty in the last two figures.

[There is a proposal, likely to become official in 2015, to give defined exact numerical values to Avogadro's and Boltzmann's constants, namely $6.022 \ 14 \times 10^{23}$ particles mole^{-1} and $1.380 \ 6 \times 10^{-23} \text{ J K}^{-1}$ per particle. This may at first seem to be somewhat akin to defining π to be exactly 3, but it is not really like that at all. It is all part of a general shift in defining many of the units used in physics in terms of fundamental physical quantities (such as the charge on the electron) rather than in terms of rods or cylinders of platinum held in Paris.]

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