

1.7 THE IDEAL GAS LAW

In the gaseous phase, the matter is in a rarefied state. In this state the interaction between molecules is often weak. If a gas is dilute, that is, if the density is low, we can completely ignore the intermolecular interactions without losing much physics. The model gas with no interaction between molecules is called the **ideal gas**. The macro-state of a given amount of gas is completely determined by its temperature T , pressure p , and volume V , which are thermodynamic variables of the system. The thermodynamic variables of an ideal gas are related by an equation called the ideal gas law,

$$\boxed{pV = nRT}, \quad (1.16)$$

where temperature T must be expressed in Kelvin. Here n denotes the number of moles of the gas and R the universal gas constant.

$$R = 8.31 \frac{\text{J}}{\text{K.mol}} \quad (1.17)$$

The number of moles n is related to the number of molecules N through Avogadro number N_A .

$$\text{Number of moles} = \frac{\text{Number of molecules}}{\text{Avogadro Number}} \implies n = \frac{N}{N_A} \quad (1.18)$$

Avogadro number has the following value.

$$N_A = 6.022 \times 10^{23} \quad (1.19)$$

Instead of the universal gas constant R one sometimes uses a related quantity called the Boltzmann constant k_B with a value of $1.38 \times 10^{-23} \text{J/K}$.

$$k_B = \frac{R}{N_A} = 1.38 \times 10^{-23} \frac{\text{J}}{\text{K}} \quad (1.20)$$

An alternate form of the ideal gas law for N molecules is as follows.

$$\boxed{pV = Nk_B T} \quad (1.21)$$

The ideal gas model of a gas assumes that the molecules of the gas occupy zero volume themselves and there is no attraction or repulsion between them. These simplifying assumptions do not hold true for real gases, such as nitrogen and oxygen, until they are very dilute or unless temperature is very high. Hence, real gases do not obey the ideal gas law except at low pressures or low densities. Instead, they are often modeled by more complicated relations such as van der Waals equation.

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \quad (1.22)$$

where a and b are positive constants, called the van der Waals constants, whose values depend on the particular substance. The Dutch physicist Johannes Diderik van der Waals proposed this equation in 1873 to take into account the effect of interaction between molecules and the non-zero size of molecules on the ideal gas equation. The quantity an^2/V^2 models the deviation in pressure from the ideal gas due to the intermolecular attraction, and the quantity nb models the net amount of volume actually occupied by the molecules themselves. Since $a > 0$, the interaction between molecules is attractive, and the correction term says that the pressure in real gases will be less than the pressure expected from the ideal gas approximation. The values of constants a and b for some common gases are listed in Table 1.4.

Table 1.4: van der Waals constants (CRC Handbook of Chemistry and Physics, 82nd Edition, 2001-2002.)

Gas	$a(\text{Pa}\cdot\text{m}^6/\text{mol}^2)$	$b(\text{m}^3/\text{mol})$
Helium	43.46×10^{-3}	2.38×10^{-5}
Hydrogen	2.452×10^{-2}	2.65×10^{-5}
Neon	2.08×10^{-1}	1.67×10^{-5}
Nitrogen	1.370	3.87×10^{-5}
Oxygen	1.382	3.19×10^{-5}
Water vapor	5.537	3.05×10^{-5}

A more general way to write the equation of state of a gas is to use a series expansion, called the virial expansion. It is written in several alternate forms, and I will write here as follows.

$$\frac{pV}{nRT} = 1 + B(T)\frac{n}{V} + C(T)\left(\frac{n}{V}\right)^2 + \cdots \quad (1.23)$$

The coefficients B , C , etc., in the virial expansion are functions of temperature and are called the second, third, etc., virial coefficients. The virial coefficients are empirically determined by fitting the virial equation to the experimental data. The ratio of pV to nRT is usually denoted by the letter Z and called the compressibility of the gas. It gives a good measure of the deviation of a gas from the ideal gas behavior. For an ideal gas $Z = 1$. It is seen that as n/V goes to zero, i.e. as the density of the gas becomes smaller, the virial expansion reduces to the ideal gas equation of state, which confirms the experimental observation that all gases behave as ideal gases at low densities.

The equation of state helps reduce the number of variables we must specify in order to describe the thermodynamic state of a system. For instance, in a gas any two of the three variables can be

independently specified and the remaining one determined by the use of the equation of state, which is a simple task for ideal gas, but may be quite tedious for real gases. Hence, to specify the state of a gas you need only indicate any of the pairs (p, V) , (p, T) or (V, T) . The list of thermodynamic variables may include other properties as well. For instance, if you have a magnetic material, your list will also include the total magnetization (M) and the magnetic field (H).

Example 1.7.1. Deciding, Ideal Gas or Real Gas? A nitrogen cylinder of fixed volume 0.01 m^3 contains 5.6 moles of gas at a temperature of 25°C . Find the pressure using (a) the ideal gas law and (b) van der Waals equation.

Solution. (a) It is easy to find the pressure using ideal gas law by simply plugging into the formula, $pV = nRT$. In the present case, we have the following known values, $V = 0.01 \text{ m}^3$, $n = 5.6$ moles, $T = 25 + 273.15 = 298.15 \text{ K}$. Note the temperature must be expressed in degrees Kelvin. Hence, the pressure in the tank as predicted by ideal gas law is

$$p = \frac{nRT}{V} = 1.39 \times 10^6 \text{ Pa}.$$

(b) We plug the known quantities given in (a) together with the van der Waals constants a and b for Nitrogen into van der Waals equation. From the table we find the van der Waals constants a and b for nitrogen in SI units are $a = 1.37 \text{ Pa}\cdot\text{m}^6/\text{mol}^2$, and $b = 3.87 \times 10^{-5} \text{ m}^3/\text{mol}$. Hence, the pressure of nitrogen as predicted by van der Waals equation is

$$p = \frac{nRT}{V - nb} - \frac{n^2a}{V^2} = 1.39 \times 10^6 \text{ Pa} - 0.43 \times 10^6 \text{ Pa} = 9.6 \times 10^5 \text{ Pa}.$$

Clearly the two predictions of the pressure in the tank are significantly different! This example illustrates that you should be careful when using ideal gas law.