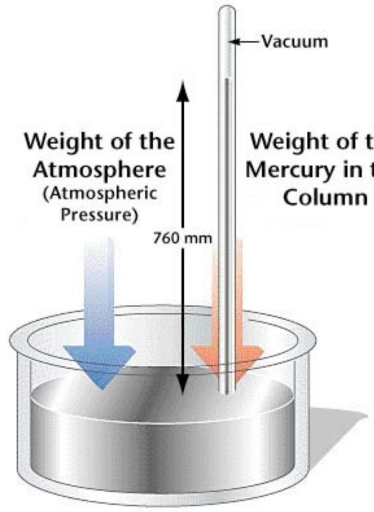
10.2.2 GASES

A gas uniformly fills any container, is easily compressed, and mixes completely with any other gas. The gases most familiar to us form the earth's atmosphere.

10.2.2.1 Pressure

One of the most obvious properties of a gas is that it exerts pressure on its surroundings. In 1643, the Italian scientist Evangelista Torricelli (1608–1647), a student of Galileo, invented the **barometer**, the instrument we use to measure the pressure of the atmosphere.



Torricelli's barometer was constructed by filling a glass tube with (liquid) mercury, and inverting it in a dish of mercury, as illustrated. Note that a large quantity of mercury stays in the tube—the pressure of the atmosphere balances the weight of the column of mercury in the tube. At sea level, the height of this column of mercury averages760 mm.

10.2.2.1.1 Units of Pressure

Pressure is a measure of a force applied over an area, and therefore has units of newtons per square metre ($N\cdot m^{-2}$). In the SI system, this is called the pascal (Pa), although atmospheric pressure is more often measured in kilopascals (kPa). A related and still commonly used unit in the imperial system is pounds per square inch (psi).

Because instruments such as the barometer and manometer, used for measuring pressure, often contain mercury, the original units for pressure were based on the height of the mercury column that the gas pressure can support. The metric unit of millimetres of mercury (mm Hg), also called the torr, in honour of Torricelli, and the imperial measure of inches of mercury, the bar (or millibar), are still commonly used, for example, in weather reports.

Another commonly used unit for pressure is the standard atmosphere (atm):

1 atm = 101.325 kPa = 14.69 psi = 760 torr = 1013 millibar

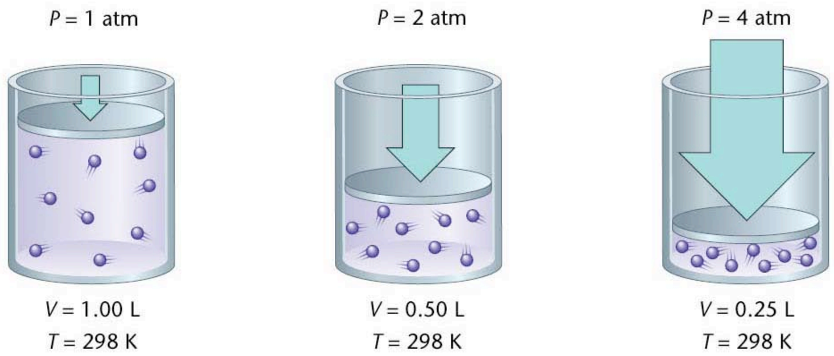
10.2.2.2 Pressure and Volume: Boyle's Law

The earliest quantitative experiments on gases were performed by the Irish chemist, Robert Boyle (1627–1691). In particular, he determined that *the product of the pressure and volume of a sample of gas, at constant temperature, is constant*:

$$PV = k$$

This relationship, known as **Boyle's Law**, means that if we know the volume of a given sample of gas, at a given pressure, we can predict the new volume if the pressure is changed, provided that neither the temperature nor the amount of gas is changed:

$$P_1V_1 = P_2V_2$$



With the benefit of modern instrumentation, we now know that Boyle's Law holds precisely only at very low pressures, although deviation is minimal for pressures around 1 atm. Nonetheless, a gas that strictly obeys Boyle's Law is known as an **ideal gas**.

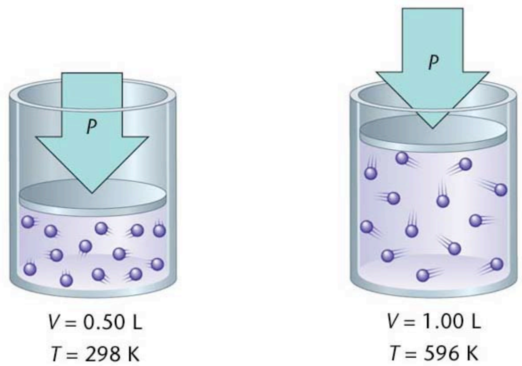
10.2.2.3 Volume and Temperature: Charles's Law

In the century following Boyle's findings, scientists continued to study the properties of gases. One of these scientists, the French physicist Jacques Charles (1746–1823), was the first to fill a balloon with hydrogen gas, and made the first solo balloon flight.

In 1787, Charles found that the volume of a gas at constant pressure increases linearly with the temperature of the gas. When the temperature is measured on the Kelvin scale, *the volume of gas is directly proportional to the temperature*, leading to the relationship:

$$V = bT$$

known as **Charles's Law** (T is in kelvins, and b is a proportionality constant).

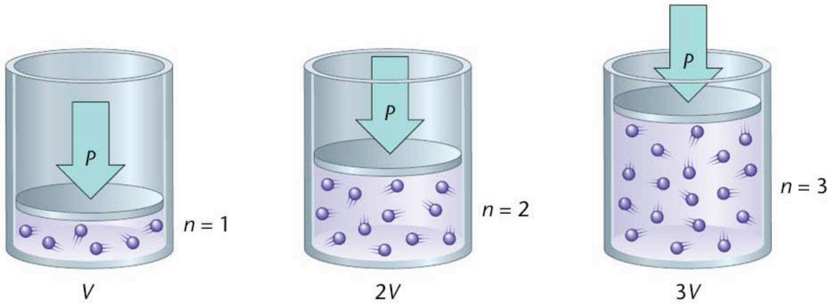


10.2.2.4 Volume and Moles: Avogadro's Law

In 1811, the Italian chemist Amadeo Avogadro postulated that equal volumes of gases at the same temperature and pressure contain the same number of "particles". Formally, **Avogardo's Law** states that *for a gas at constant temperature and pressure, the volume is directly proportional to the number of moles of gas*, or mathematically:

$$V = an$$

where V is the volume of the gas, n is the number of moles of gas particles, and a is a proportionality constant.



10.2.2.5 The Ideal Gas Law

We can summarise the above as follows:

Boyle's Law	$V = \frac{k}{P}$	(at constant T and n)
Charles's Law	$V = bT$	(at constant P and n)
Avogadro's Law	$V = an$	(at constant T and P)

The combination of these three relationships, which show how the volume of a gas depends on pressure, temperature, and number of molecules of gas present, is known as the **Ideal Gas Law**:

$$PV = nRT$$

When pressure is expressed in atmospheres (atm) and volume in litres (L), R, known as the **universal gas constant**, has the value:

$$R = 0.08206 \ \frac{\mathrm{L \cdot atm}}{\mathrm{K \cdot mol}}$$

A gas that obeys this law is said to behave *ideally*. That is, the equation defines the behaviour of an **ideal gas**. Most gases obey this law closely at pressures of 1 atm or lower, at temperatures of 0 °C or higher.

10.2.2.6 Dalton's Law of Partial Pressures

Among the experiments that led John Dalton to propose his atomic theory were his studies of mixtures of gases. In 1803, Dalton summarised his observations as follows:

For a mixture of gases in a container, the total pressure exerted is the sum of the pressures that each gas would exert if it were alone.

This statement, known as **Dalton's Law of Partial Pressures**, can be expressed as follows:

$$P_{total} = P_1 + P_2 + P_3 + \cdots$$

where the subscripts refer to the individual gases. The symbols P_1, P_2, P_3 etc. represent each partial pressure, the pressure that a particular gas would exert if it were alone in the container.

Assuming that each gas behaves ideally, we can calculate the partial pressure of each gas from the Ideal Gas Law:

$$\begin{aligned} P_{total} &= P_1 + P_2 + P_3 = \frac{n_1RT}{V} + \frac{n_2RT}{V} + \frac{n_3RT}{V} \\ &= n_1\left(\frac{RT}{V}\right) + n_2\left(\frac{RT}{V}\right) + n_3\left(\frac{RT}{V}\right) \\ &= (n_1 + n_2 + n_3)\left(\frac{RT}{V}\right) \\ &= n_{total}\left(\frac{RT}{V}\right) \end{aligned}$$

where n_{total} is the sum of the numbers of moles of the gases in the mixture. Thus, for a mixture of ideal gases, it is the *total number of moles of particles* that is important, not the *identity* of the individual gas particles. This tells us two important things about ideal gases:

1. The volume of the individual gas particle (atom or molecule) must not be very important;
2. The forces between the particles must not be very important.

10.2.2.7 The Kinetic Molecular Theory of Gases

The postulates (assumptions) of the Kinetic Molecular Theory (KMT) as they relate to the particles of an ideal gas can be stated as follows:

1. Gases consist of tiny particles (atoms or molecules);
2. The particles are so small, compared with the distances between them, that the volume (size) of the individual particles can be assumed to be negligible (zero);
3. The particles are in constant, random motion. The collisions of the particles with the walls of the container are the cause of the pressure exerted by the gas;
4. The particles are assumed to exert no forces on each other; they are assumed not to attract or to repel each other;
5. The average kinetic energy of a collection of gas particles is assumed to be directly proportional to the Kelvin temperature of the gas.

Of course, the molecules of a *real gas* have finite volumes and do exert forces on each other. Thus, real gases do not conform to these assumptions. The true test of a model, however, is how well its predictions fit experimental observations, and we will see that these postulates do indeed explain the behaviour of *ideal gases*.

10.2.2.7.1 The Implications of the Kinetic Molecular Theory

The meaning of Temperature

As stated in postulate 5. above, the temperature of a gas reflects how rapidly, on average, the individual particles of the gas are moving. At high temperatures, the particles move very quickly, hitting the walls of the container frequently, while at low temperatures the particles' motions are more sluggish and they collide with the walls of the container much less often.

Temperature then, is a measure of the motions of the gas particles. In fact, the Kelvin temperature of a gas is directly proportional to the average kinetic energy of the gas particles.

The Relationship between Pressure and Temperature

As the temperature of gas particles increases, the particles move more quickly, hitting the walls of their container more frequently and more forcefully. Thus, if pressure is due to collisions of gas particles with the walls of their container, the pressure will increase with increasing temperature.

The Relationship between Volume and Temperature

Pressure is defined as a force acting over an area ($P = F/A$). If the temperature of gas particles is increased, they strike the walls of their container with greater force. Thus, to maintain a constant pressure, under conditions of increasing temperature, the (surface) area of the container must also increase. If the surface area of the container increases, then so too will its volume.

Thus, under conditions of constant pressure, the volume of a gas will increase as the temperature of the gas increases.

10.2.2.8 Gas Stoichiometry

Suppose that we have 1 mole of an ideal gas at 0 °C (273.2 K) and 1 atm. From the Ideal Gas Law, the volume of the gas is given by:

$$V = \frac{nRT}{P} = \frac{(1.000\ \text{mol})(0.08206\ \text{L} \cdot \text{atm/K} \cdot \text{mol})(273.2\ \text{K})}{1.000\ \text{atm}} = 22.42\ \text{L}$$

The volume of 22.42 litres is the **molar volume** of an ideal gas (at 0 °C and 1 atm).

The conditions 0 °C and 1 atm, called **standard temperature and pressure** (STP), are common reference conditions for the properties of gases.

References

Introductory Chemistry—A Foundation (6th Ed), Zumdahl, S.S. and DeCoste, D.J. (Houghton Mifflin, 2009) [ISBN 13: 978-0-618-80327-9]

Work directly from text, with exercises:

Chapter 13 Gases