Combined & Ideal Gas Laws

Ideal gas laws

The equations presented in the previous chapter for Amonton's, Charles's, Boyle's, and Avogadro's Laws are all special cases of the ideal gas law, PV = nRT, where P is the pressure of the gas, V is its volume, n is the number of moles of the gas, T is its kelvin temperature, and R is the ideal (universal) gas constant. The ideal gas law can be used to derive a number of convenient equations relating directly measured quantities to properties of interest for gaseous substances and mixtures. Appropriate rearrangement of the ideal gas equation may be made to permit the calculation of gas densities and molar masses.

24.1 The Ideal Gas Law

Learning Objectives

 Use the ideal gas law, and related gas laws, to compute the values of various gas properties under specified conditions

To this point, four separate laws have been discussed that relate pressure, volume, temperature, and the number of moles of the gas:

- Boyle's law: PV = constant at constant T and n
- Amontons's law: $\frac{P}{T}$ = constant at constant V and n
- Charles's law: $\frac{V}{T}$ = constant at constant P and n
- Avogadro's law: $\frac{V}{\pi}$ = constant at constant P and T

Combining these four laws yields the ideal gas law, a relation between the pressure, volume, temperature, and number of moles of a gas:

$$PV = nRT$$

where P is the pressure of a gas, V is its volume, n is the number of moles of the gas, T is its temperature on the kelvin scale, and R is a constant called the ideal gas constant or the universal gas constant. The units used to express

pressure, volume, and temperature will determine the proper form of the gas constant as required by dimensional analysis, the most commonly encountered values being 0.08206 L atm mol⁻¹ K⁻¹ and 8.314 kPa L mol⁻¹ K⁻¹.

Gases whose properties of *P*, *V*, and *T* are accurately described by the ideal gas law (or the other gas laws) are said to exhibit *ideal behavior* or to approximate the traits of an ideal gas. An ideal gas is a hypothetical construct that may be used along with *kinetic molecular theory* to effectively explain the gas laws as will be described in a later module of this chapter. Although all the calculations presented in this module assume ideal behavior, this assumption is only reasonable for gases under conditions of relatively low pressure and high temperature. In the final module of this chapter, a modified gas law will be introduced that accounts for the *non-ideal* behavior observed for many gases at relatively high pressures and low temperatures.

The ideal gas equation contains five terms, the gas constant *R* and the variable properties *P*, *V*, *n*, and *T*. Specifying any four of these terms will permit use of the ideal gas law to calculate the fifth term as demonstrated in the following example exercises.

Using the Ideal Gas Law

Methane, CH_4 , is being considered for use as an alternative automotive fuel to replace gasoline. One gallon of gasoline could be replaced by 655 g of CH_4 . What is the volume of this much methane at 25 °C and 745 torr? Solution

We must rearrange PV = nRT to solve for V:

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

If we choose to use R = 0.08206 L atm mol⁻¹ K⁻¹, then the amount must be in moles, temperature must be in kelvin, and pressure must be in atm.

Converting into the "right" units:

$$n = 6.55 \text{ g CH}_4 \times \frac{1 \text{ mol}}{16.043 \text{ g CH}_4} = 40.8 \text{ mol}$$

$$T = 25 \,^{\circ}\text{C} + 273 = 298 \,^{\circ}\text{K}$$

$$P = 745 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.980 \text{ atm}$$

$$V = \frac{nRT}{P} = \frac{(40.8 \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{0.980 \text{ atm}} = 1.02 \times 10^3 \text{ L}$$

It would require 1020 L (269 gal) of gaseous methane at about 1 atm of pressure to replace 1 gal of gasoline. It requires a large container to hold enough methane at 1 atm to replace several gallons of gasoline.

Check Your Learning

Calculate the pressure in bar of 2520 moles of hydrogen gas stored at 27 °C in the 180-L storage tank of a modern hydrogen-powered car.

Answer

350 bar

If the number of moles of an ideal gas are kept constant under two different sets of conditions, a useful mathematical relationship called the combined gas law is obtained:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

using units of atm, L, and K. Both sets of conditions are equal to the product of \boldsymbol{n}

X

R (where n = the number of moles of the gas and R is the ideal gas law constant).

Using the Combined Gas Law

When filled with air, a typical scuba tank with a volume of 13.2 L has a pressure of 153 atm (<u>Figure 24.1</u>). If the water temperature is 27 °C, how many liters of air will such a tank provide to a diver's lungs at a depth of approximately 70 feet in the ocean where the pressure is 3.13 atm?

Figure 24.1

Scuba divers use compressed air to breathe while underwater. (credit: modification of work by Mark Goodchild)



Letting 1 represent the air in the scuba tank and 2 represent the air in the lungs, and noting that body temperature (the temperature the air will be in the lungs) is 37 °C, we have:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \longrightarrow \frac{(153 \text{ atm})(13.2 \text{ L})}{(300 \text{ K})} = \frac{(3.13 \text{ atm})(V_2)}{(310 \text{ K})}$$

Solving for V_2 :

$$V_2 = \frac{(153 \text{ atm})(13.2 \text{ L})(310 \text{ K})}{(300 \text{ K})(3.13 \text{ atm})} = 667 \text{ L}$$

(Note: Be advised that this particular example is one in which the assumption of ideal gas behavior is not very reasonable, since it involves gases at relatively high pressures and low temperatures. Despite this limitation, the

calculated volume can be viewed as a good "ballpark" estimate.)

Check Your Learning

A sample of ammonia is found to occupy 0.250 L under laboratory conditions of 27 °C and 0.850 atm. Find the volume of this sample at 0 °C and 1.00 atm.

Answer

0.193 L

Chemistry in Everday Life

The Interdependence between Ocean Depth and Pressure in Scuba Diving

Whether scuba diving at the Great Barrier Reef in Australia (shown in <u>Figure 24.2</u>) or in the Caribbean, divers must understand how pressure affects a number of issues related to their comfort and safety.

Figure 24.2

Scuba divers, whether at the Great Barrier Reef or in the Caribbean, must be aware of buoyancy, pressure equalization, and the amount of time they spend underwater, to avoid the risks associated with pressurized gases in the body. (credit: Kyle Taylor)



Pressure increases with ocean depth, and the pressure changes most rapidly as divers reach the surface. The pressure a diver experiences is the sum of all pressures above the diver (from the water and the air). Most pressure measurements are given in units of atmospheres, expressed as "atmospheres absolute" or ATA in the diving community: Every 33 feet of salt water represents 1 ATA of pressure in addition to 1 ATA of pressure from the atmosphere at sea level. As a diver descends, the increase in pressure causes the body's air pockets in the ears and lungs to compress; on the ascent, the decrease in pressure causes these air pockets to expand, potentially rupturing eardrums or bursting the lungs. Divers must therefore undergo equalization by adding air to body airspaces on the descent by breathing normally and adding air to the mask by breathing out of the nose or adding air to the ears and sinuses by equalization techniques; the corollary is also true on ascent, divers must release air from the body to maintain equalization. Buoyancy, or the ability to control whether a diver sinks or floats, is controlled by the buoyancy compensator (BCD). If a diver is ascending, the air in their BCD expands because of lower pressure according to Boyle's law (decreasing the pressure of gases increases the volume). The expanding air increases the buoyancy of the diver, and they begin to ascend. The diver must vent air from

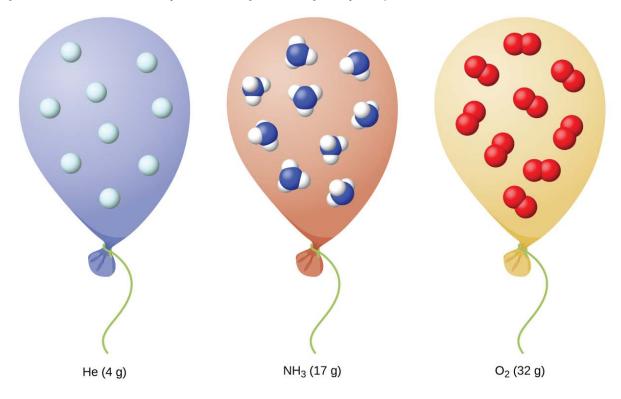
the BCD or risk an uncontrolled ascent that could rupture the lungs. In descending, the increased pressure causes the air in the BCD to compress and the diver sinks much more quickly; the diver must add air to the BCD or risk an uncontrolled descent, facing much higher pressures near the ocean floor. The pressure also impacts how long a diver can stay underwater before ascending. The deeper a diver dives, the more compressed the air that is breathed because of increased pressure: If a diver dives 33 feet, the pressure is 2 ATA and the air would be compressed to one-half of its original volume. The diver uses up available air twice as fast as at the surface.

Standard Conditions of Temperature and Pressure

We have seen that the volume of a given quantity of gas and the number of molecules (moles) in a given volume of gas vary with changes in pressure and temperature. Chemists sometimes make comparisons against a standard temperature and pressure (STP) for reporting properties of gases: 273.15 K and 1 atm (101.325 kPa). At STP, one mole of an ideal gas has a volume of about 22.4 L—this is referred to as the standard molar volume (Figure 24.3).

Figure 24.3

Regardless of its chemical identity, one mole of gas behaving ideally occupies a volume of ~22.4 L at STP.



Link to Supplemental Exercises

<u>Supplemental exercises</u> are available if you would like more practice with these concepts.

24.2 Stoichiometry of Gaseous Substances, Mixtures, and Reactions

Learning Objectives

By the end of this section, you will be able to:

· Use the ideal gas law to compute gas densities and molar masses

The study of the chemical behavior of gases was part of the basis of perhaps the most fundamental chemical revolution in history. French nobleman Antoine Lavoisier, widely regarded as the "father of modern chemistry," changed chemistry from a qualitative to a quantitative science through his work with gases. He discovered the law of conservation of matter, discovered the role of oxygen in combustion reactions, determined the composition of air, explained respiration in terms of chemical reactions, and more. He was a casualty of the French Revolution, guillotined in 1794. Of his death, mathematician and astronomer Joseph-Louis Lagrange said, "It took the mob only a moment to remove his head; a century will not suffice to reproduce it." Much of the knowledge we do have about Lavoisier's contributions is due to his wife, Marie-Anne Paulze Lavoisier, who worked with him in his lab. A trained artist fluent in several languages, she created detailed illustrations of the equipment in his lab, and translated texts from foreign scientists to complement his knowledge. After his execution, she was instrumental in publishing Lavoisier's major treatise, which unified many concepts of chemistry and laid the groundwork for significant further study.

As described in an earlier chapter of this text, we can turn to chemical stoichiometry for answers to many of the questions that ask "How much?" The essential property involved in such use of stoichiometry is the amount of substance, typically measured in moles (*n*). For gases, molar amount can be derived from convenient experimental measurements of pressure, temperature, and volume. Therefore, these measurements are useful in assessing the stoichiometry of pure gases, gas mixtures, and chemical reactions involving gases. This section will not introduce any new material or ideas, but will provide examples of applications and ways to integrate concepts we have already discussed.

Gas Density and Molar Mass

The ideal gas law described previously in this chapter relates the properties of pressure *P*, volume *V*, temperature *T*, and molar amount *n*. This law is universal, relating these properties in identical fashion regardless of the chemical identity of the gas:

$$PV = nRT$$

The density *d* of a gas, on the other hand, is determined by its identity. As described in another chapter of this text, the density of a substance is a characteristic property that may be used to identify the substance.

$$d = \frac{m}{V}$$

Rearranging the ideal gas equation to isolate V and substituting into the density equation yields

$$d = \frac{mP}{nRT} = (\frac{m}{n})\frac{P}{RT}$$

The ratio m/n is the definition of molar mass, M.

$$\mathcal{M} = \frac{m}{n}$$

The density equation can then be written

$$d = \frac{MP}{RT}$$

This relation may be used for calculating the densities of gases of known identities at specified values of pressure and temperature as demonstrated in Example 24.3.

Example 24.3

Measuring Gas Density

What is the density of molecular nitrogen gas at STP?

Solution

The molar mass of molecular nitrogen, N_2 , is 28.01 g/mol. Substituting this value along with standard temperature and pressure into the gas density equation yields

$$d = \frac{MP}{RT} = \frac{(28.01 \text{ g/mol})(1.00 \text{ atm})}{(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(273 \text{ K})} = 1.25 \text{ g/L}$$

Check Your Learning

What is the density of molecular hydrogen gas at 17.0 °C and a pressure of 760 torr?

Answer

d = 0.0847 g/L

When the identity of a gas is unknown, measurements of the mass, pressure, volume, and temperature of a sample can be used to calculate the molar mass of the gas (a useful property for identification purposes). Combining the ideal gas equation

$$PV = nRT$$

and the definition of molar mass

$$\mathcal{M} = \frac{m}{n}$$

yields the following equation:

$$\mathcal{M} = \frac{mRT}{PV}$$

Determining the molar mass of a gas via this approach is demonstrated in Example 24.4

Determining the Molecular Formula of a Gas from its Molar Mass and Empirical Formula

Cyclopropane, a gas once used with oxygen as a general anesthetic, is composed of 85.7% carbon and 14.3% hydrogen by mass. Find the empirical formula. If 1.56 g of cyclopropane occupies a volume of 1.00 L at 0.984 atm and 50 °C, what is the molecular formula for cyclopropane?

Solution

First determine the empirical formula of the gas. Assume 100 g and convert the percentage of each element into grams. Determine the number of moles of carbon and hydrogen in the 100-g sample of cyclopropane. Divide by the smallest number of moles to relate the number of moles of carbon to the number of moles of hydrogen. In the last step, realize that the smallest whole number ratio is the empirical formula:

85.7 g C ×
$$\frac{1 \text{ mol C}}{12.01 \text{ g C}}$$
 = 7.136 mol C $\frac{7.136}{7.136}$ = 1.00 mol C

$$14.3 \text{ g H} \times \frac{1 \text{ mol H}}{1.01 \text{ g H}} = 14.158 \text{ mol H}$$
 $\frac{14.158}{7.136} = 1.98 \text{ mol H}$

Empirical formula is CH₂ [empirical mass (EM) of 14.03 g/empirical unit].

Next, use the provided values for mass, pressure, temperature and volume to compute the molar mass of the gas:

$$\mathcal{M} = \frac{mRT}{PV} = \frac{(1.56 \text{ g})(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(323 \text{ K})}{(0.984 \text{ atm})(1.00 \text{ L})} = 42.0 \text{ g/mol}$$

Comparing the molar mass to the empirical formula mass shows how many empirical formula units make up a molecule:

$$\frac{M}{EM} = \frac{42.0 \text{ g/mol}}{14.0 \text{ g/mol}} = 3$$

The molecular formula is thus derived from the empirical formula by multiplying each of its subscripts by three:

$$(CH_2)_3 = C_3 H_6$$

Check Your Learning

Acetylene, a fuel used welding torches, is composed of 92.3% C and 7.7% H by mass. Find the empirical formula. If 1.10 g of acetylene occupies of volume of 1.00 L at 1.15 atm and 59.5 °C, what is the molecular formula for acetylene?

Answer

Empirical formula, CH; Molecular formula, C₂H₂

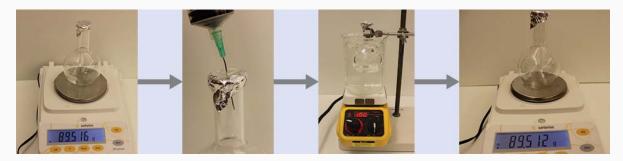
Determining the Molar Mass of a Volatile Liquid

The approximate molar mass of a volatile liquid can be determined by:

- 1. Heating a sample of the liquid in a flask with a tiny hole at the top, which converts the liquid into gas that may escape through the hole
- 2. Removing the flask from heat at the instant when the last bit of liquid becomes gas, at which time the flask will be filled with only gaseous sample at ambient pressure
- 3. Sealing the flask and permitting the gaseous sample to condense to liquid, and then weighing the flask to determine the sample's mass (see <u>Figure 24.4</u>)

Figure 24.4

When the volatile liquid in the flask is heated past its boiling point, it becomes gas and drives air out of the flask. At $t_{l \to g}$, the flask is filled with volatile liquid gas at the same pressure as the atmosphere. If the flask is then cooled to room temperature, the gas condenses and the mass of the gas that filled the flask, and is now liquid, can be measured. (credit: modification of work by Mark Ott)



Using this procedure, a sample of chloroform gas weighing 0.494 g is collected in a flask with a volume of 129 cm³ at 99.6 °C when the atmospheric pressure is 742.1 mm Hg. What is the approximate molar mass of chloroform?

Solution

Since

$$\mathcal{M} = \frac{m}{n}$$

and

$$n = \frac{PV}{RT}$$

substituting and rearranging gives

$$\mathcal{M} = \frac{mRT}{PV}$$
,

then

$$\mathcal{M} = \frac{mRT}{PV} = \frac{(0.494 \text{ g}) \times 0.08206 \text{ L} \cdot \text{atm/mol K} \times 372.8 \text{ K}}{0.976 \text{ atm} \times 0.129 \text{ L}} = 120 \text{ g/mol}.$$

Check Your Learning

A sample of phosphorus that weighs 3.243

×

 10^{-2} g exerts a pressure of 31.89 kPa in a 56.0-mL bulb at 550 °C. What are the molar mass and molecular formula of phosphorus vapor?

Answer

124 g/mol P₄

Link to Supplemental Exercises

<u>Supplemental exercises</u> are available if you would like more practice with these concepts.

Footnotes

- 1. The IUPAC definition of standard pressure was changed from 1 atm to 1 bar (100 kPa) in 1982, but the prior definition remains in use by many literature resources and will be used in this text.
- 2. "Quotations by Joseph-Louis Lagrange," last modified February 2006, accessed February 10, 2015, http://www-history.mcs.st-andrews.ac.uk/Quotations/Lagrange.html

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Previous Citation(s)

Flowers, P., Neth, E. J., Robinson, W. R., Theopold, K., & Langley, R. (2019). Chemistry in Context. In Chemistry: Atoms First 2e. OpenStax. https://openstax.org/books/chemistry-atoms-first-2e/pages/8-introduction





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