Chemistry, The Central Science, 11th edition
Theodore L. Brown; H. Eugene LeMay, Jr.; and Bruce E. Bursten

Chapter 10
Gases

Dr. Ayman Nafady

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By Theodore E. Brown, H. Eugene LeMay, Bruce E. Bursten, and Catherine J. Murphy
With contributions from Patrick Woodward

10.1. Characteristics of Gases

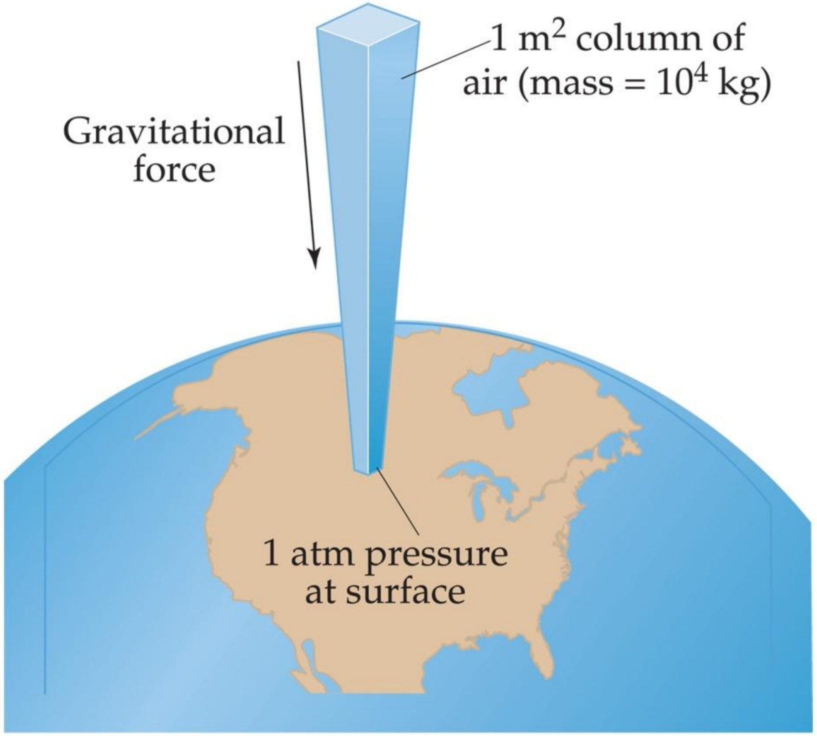
- **Unlike liquids and solids, gases**
  - expand to fill their containers;
  - are highly compressible;
  - have extremely low densities.

Pressure

- Pressure is the amount of force applied to an area.

$$P = \frac{F}{A}$$

- Atmospheric pressure is the weight of air per unit of area.

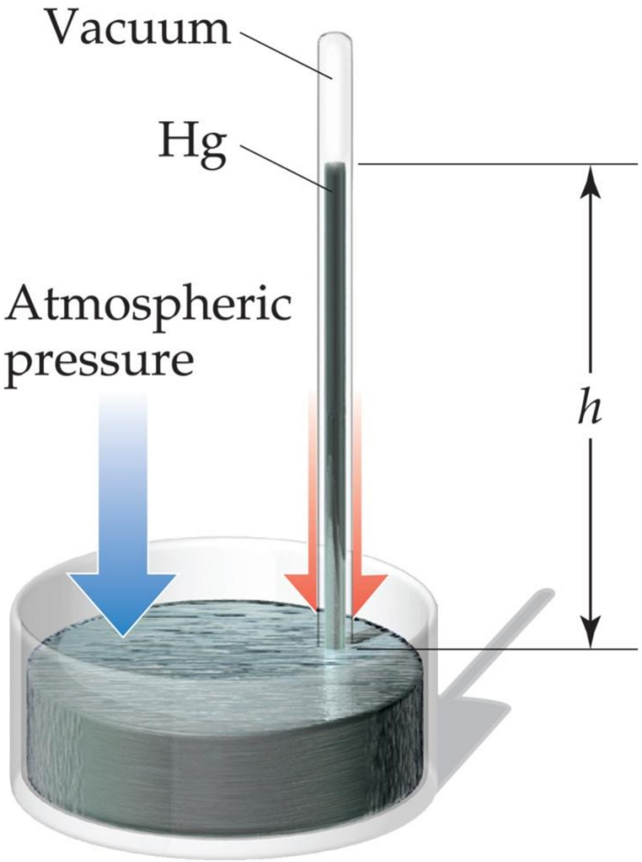


Units of Pressure

- Pascals
  - $1\ \mathrm{Pa} = 1\ \mathrm{N/m^2}$
- Bar
  - $1\ \mathrm{bar} = 10^5\ \mathrm{Pa} = 100\ \mathrm{kPa}$

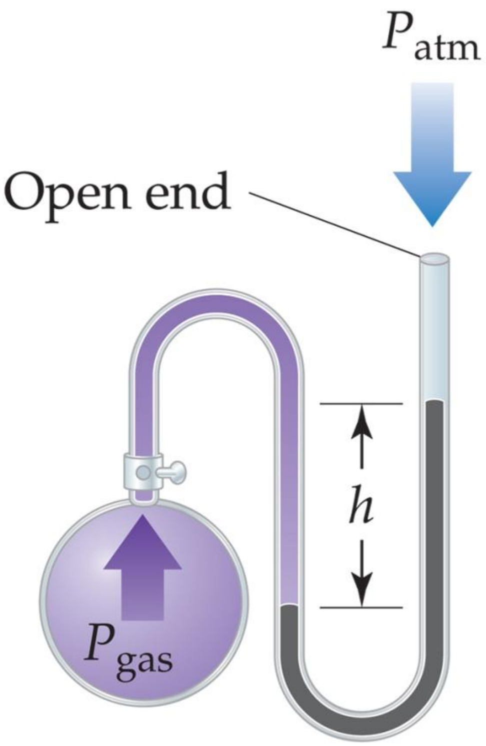
Units of Pressure

- mm Hg or torr
  - –These units are literally the difference in the heights measured in mm (*h*) of two connected columns of mercury.



- Atmosphere
  - –1.00 atm = 760 torr

Manometer



$$P_{gas} = P_{atm} + P_h$$

This device is used to measure the difference in pressure between atmospheric pressure and that of a gas in a vessel.

Standard Pressure

- Normal atmospheric pressure at sea level is referred to as standard pressure.

- It is equal to
  - 1.00 atm
  - 760 torr (760 mm Hg)
  - 101.325 kPa

Sample Exercise 10.1 Converting Units of Pressure

(a) Convert 0.357 atm to torr. **(b)** Convert 6.6×10^{-2} torr to atm. **(c)** Convert 147.2 kPa to torr.

Solution

Analyze: In each case we are given the pressure in one unit and asked to convert it to another unit. Our task, therefore, is to choose the appropriate conversion factors.
Plan: We can use dimensional analysis to perform the desired conversions.

(a) To convert atmospheres to torr, we use the relationship 760 torr = 1 atm:

$$(0.357\ \cancel{\text{atm}})\left(\frac{760\ \text{torr}}{1\ \cancel{\text{atm}}}\right) = 271\ \text{torr}$$

Note that the units cancel in the required manner.

(b) We use the same relationship as in part (a). To get the appropriate units to cancel, we must use the conversion factor as follows:

$$(6.6 \times 10^{-2}\ \cancel{\text{torr}})\left(\frac{1\ \text{atm}}{760\ \cancel{\text{torr}}}\right) = 8.7 \times 10^{-5}\ \text{atm}$$

(c) The relationship 760 torr = 101.325 kPa allows us to write an appropriate conversion factor for this problem:

$$(147.2\ \cancel{\text{kPa}})\left(\frac{760\ \text{torr}}{101.325\ \cancel{\text{kPa}}}\right) = 1104\ \text{torr}$$

Check: In each case look at the magnitude of the answer and compare it with the starting value. The torr is a much smaller unit than the atmosphere, so we expect the *numerical* answer to be larger than the starting quantity in (a) and smaller in (b). In (c) notice that there are nearly 8 torr per kPa, so the numerical answer in torr should be about 8 times larger than its value in kPa, consistent with our calculation.

Sample Exercise 10.1 Converting Units of Pressure

Practice Exercise

(a) In countries that use the metric system, such as Canada, atmospheric pressure in weather reports is given in units of kPa. Convert a pressure of 745 torr to kPa. **(b)** An English unit of pressure sometimes used in engineering is pounds per square inch ($lb/in.^2$), or psi: 1 atm = 14.7 $lb/in.^2$. If a pressure is reported as 91.5 psi, express the measurement in atmospheres.
Answer: **(a)** 99.3 kPa, **(b)** 6.22 atm

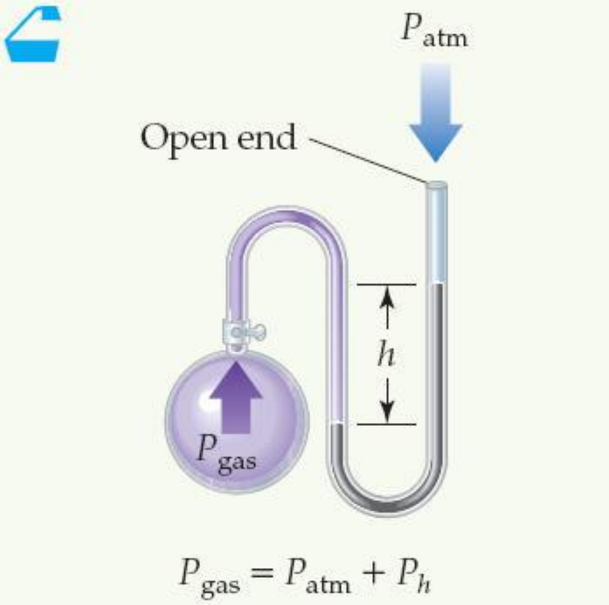
---

1) A gas at a pressure of 10.0 Pa exerts a force of __________ N on an area of

A) 55
B) 0.55
C) 5.5
D) 1.8
E) 18
Answer: A

Sample Exercise 10.2 Using a Manometer to Measure Gas Pressure

On a certain day the barometer in a laboratory indicates that the atmospheric pressure is 764.7 torr. A sample of gas is placed in a flask attached to an open-end mercury manometer, shown in Figure 10.3. A meter stick is used to measure the height of the mercury above the bottom of the manometer. The level of mercury in the open-end arm of the manometer has a height of 136.4 mm, and the mercury in the arm that is in contact with the gas has a height of 103.8 mm. What is the pressure of the gas **(a)** in atmospheres, **(b)** in kPa?



▲ Figure 10.3 **A mercury manometer.** This device is sometimes employed in the laboratory to measure gas pressures near atmospheric pressure.

Solution

Analyze: We are given the atmospheric pressure (764.7 torr) and the heights of the mercury in the two arms of the manometer and asked to determine the gas pressure in the flask. We know that this pressure must be greater than atmospheric because the manometer level on the flask side (103.8 mm) is lower than that on the side open to the atmosphere (136.4 mm), as indicated in Figure 10.3.

Sample Exercise 10.2 Using a Manometer to Measure Gas Pressure

Solution (continued)

Plan: We will use the difference in height between the two arms (*h* in Figure 10.3) to obtain the amount by which the pressure of the gas exceeds atmospheric pressure. Because an open-end mercury manometer is used, the height difference directly measures the pressure difference in mm Hg or torr between the gas and the atmosphere.

Solve:

(a) The pressure of the gas equals the atmospheric pressure plus *h*:

$$\begin{aligned} P_{\text{gas}} &= P_{\text{atm}} + h \\ &= 764.7\ \text{torr} + (136.4\ \text{torr} - 103.8\ \text{torr}) \\ &= 797.3\ \text{torr} \end{aligned}$$

We convert the pressure of the gas to atmospheres:

$$P_{\text{gas}} = (797.3\ \text{torr})\left(\frac{1\ \text{atm}}{760\ \text{torr}}\right) = 1.049\ \text{atm}$$

(b) To calculate the pressure in kPa, we employ the conversion factor between atmospheres and kPa:

$$1.049\ \text{atm}\left(\frac{101.3\ \text{kPa}}{1\ \text{atm}}\right) = 106.3\ \text{kPa}$$

Check: The calculated pressure is a bit more than one atmosphere. This makes sense because we anticipated that the pressure in the flask would be greater than the pressure of the atmosphere acting on the manometer, which is a bit greater than one standard atmosphere.

Practice Exercise

Convert a pressure of 0.975 atm into Pa and kPa.

Answer: 9.88×10^4 Pa and 98.8 kPa

2nd lecture on gas laws

- Boyle's law
- Charles' law
- Avogadro's law

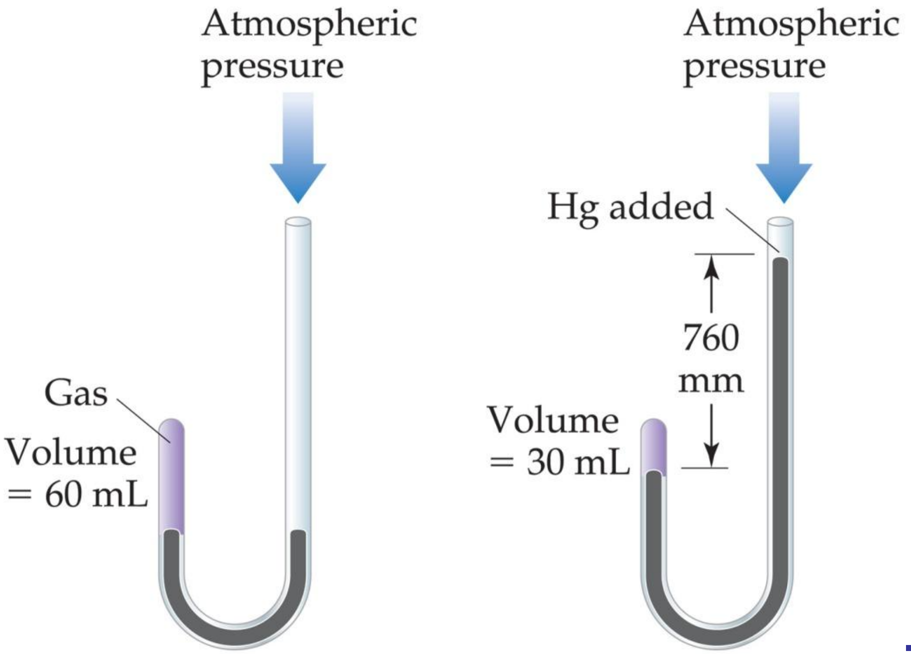
Standard Pressure

- Normal atmospheric pressure at sea level is referred to as standard pressure.

- It is equal to
  - 1.00 atm
  - 760 torr (760 mm Hg)
  - 101.325 kPa

Boyle's Law

The volume of a fixed quantity of gas at constant temperature is inversely proportional to the pressure.



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As *P* and *V* are inversely proportional

A plot of *V* versus *P* results in a curve.

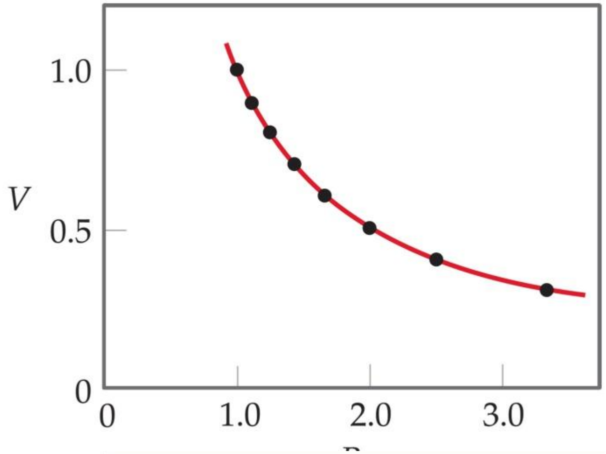
Since

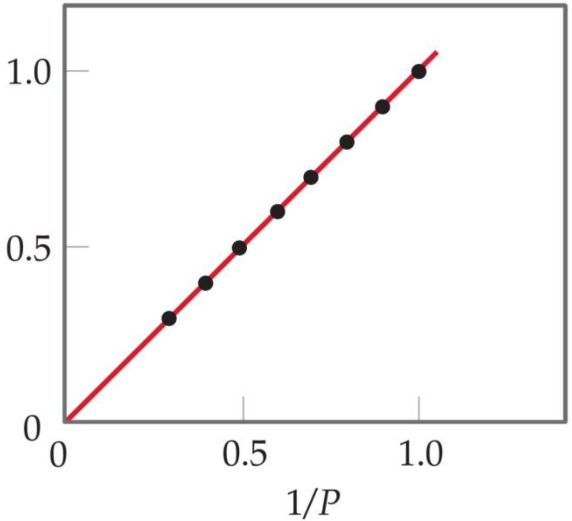
$$PV = k$$

$$V = k\,(1/P)$$

This means a plot of *V* versus 1/*P* will be a straight line.

$$\mathbf{P_1V_1 = P_2V_2}$$

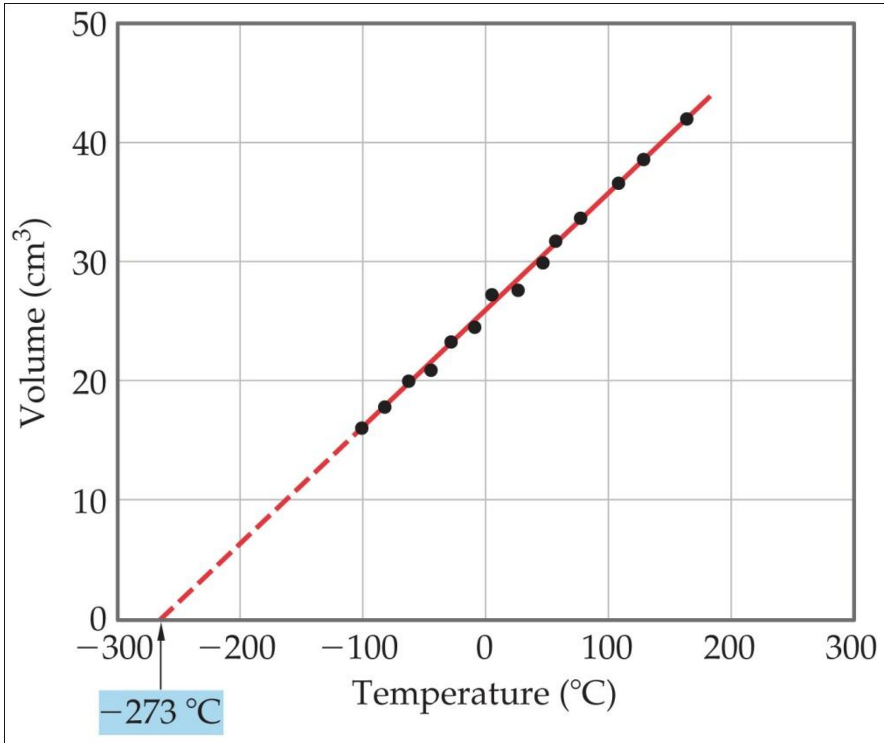




Charles’s Law

- The volume of a fixed amount of gas at constant pressure is directly proportional to its absolute temperature.
  - i.e., $\frac{V}{T} = k$

$$T_2V_1 = T_1V_2$$



A plot of *V* versus *T* will be a straight line.

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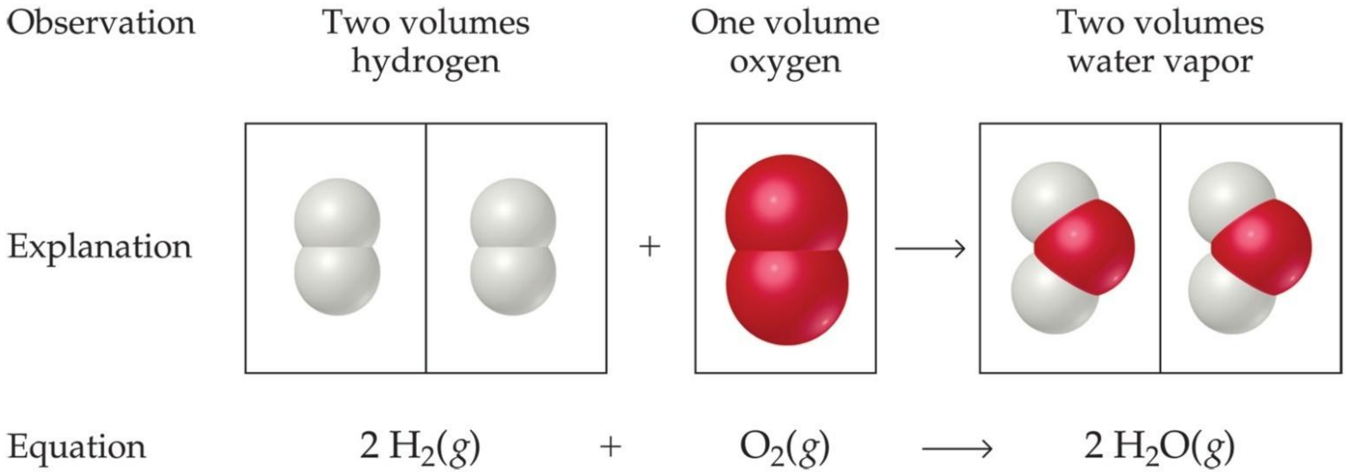
Avogadro’s Law

- The volume of a gas at constant temperature and pressure is directly proportional to the number of moles of the gas.
- Mathematically, this means $V = kn$



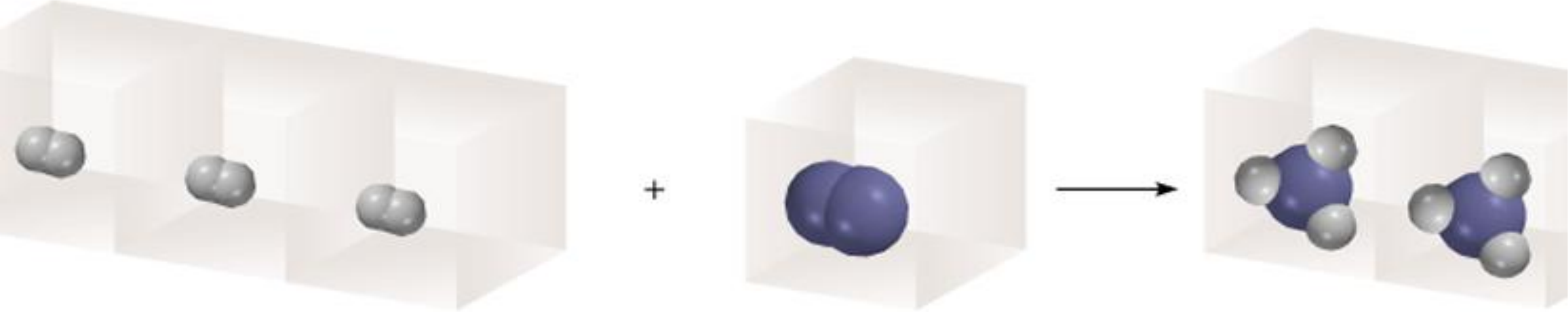
Avogadro's Law

$V \propto$ number of moles (n)

$V =$ constant x n

$V_1/n_1 = V_2/n_2$

Constant temperature
Constant pressure



$3H_2\ (g)$	+	$N_2\ (g)$	$\longrightarrow$	$2NH_3\ (g)$
3 molecules	+	1 molecule	$\longrightarrow$	2 molecules
3 moles	+	1 mole	$\longrightarrow$	2 moles
3 volumes	+	1 volume	$\longrightarrow$	2 volumes

Ideal-Gas Equation

- So far we've seen that

$$V \propto 1/P \quad \text{(Boyle's law)}$$
$$V \propto T \quad \text{(Charles's law)}$$
$$V \propto n \quad \text{(Avogadro's law)}$$

- Combining these, we get

$$V \propto \frac{nT}{P}$$

Ideal-Gas Equation

The relationship

$$V \propto \frac{nT}{P}$$

then becomes

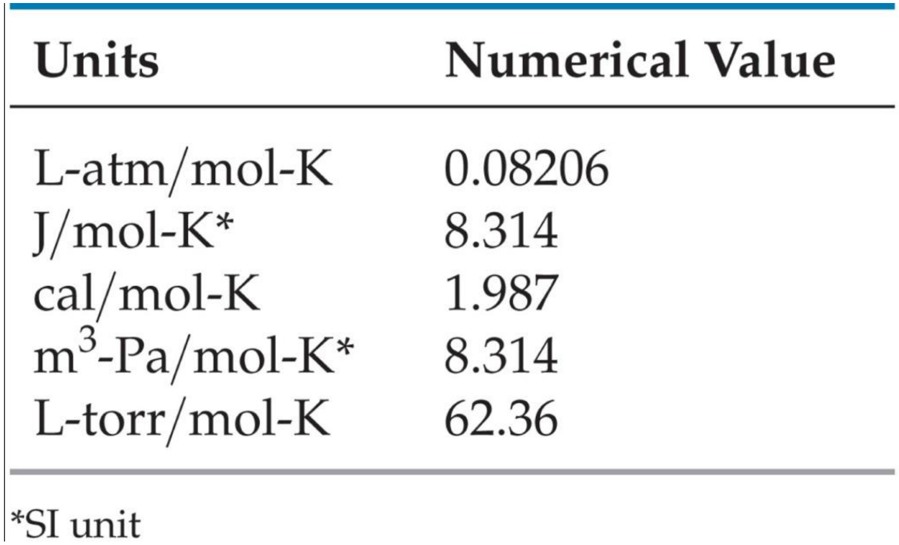
$$V = R\frac{nT}{P}$$

or

$$PV = nRT$$

Ideal-Gas Equation

The constant of proportionality is known as *R*, the gas constant.

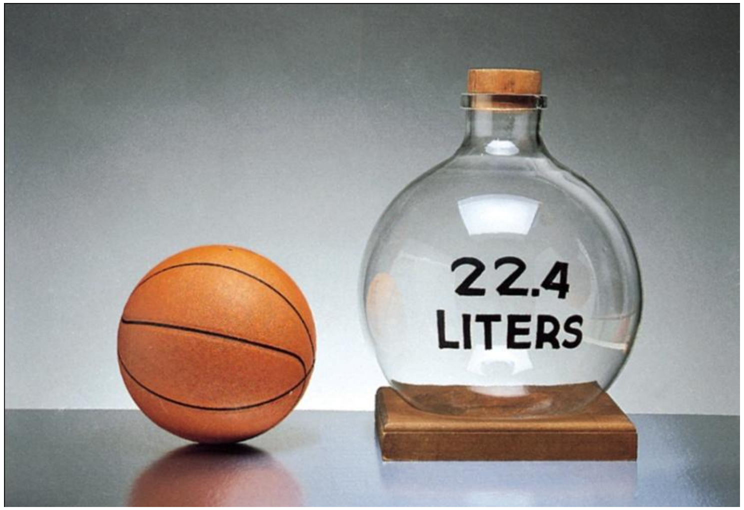


Units	Numerical Value
L-atm/mol-K	0.08206
J/mol-K*	8.314
cal/mol-K	1.987
m^3-Pa/mol-K*	8.314
L-torr/mol-K	62.36

*SI unit

The conditions 0 ^{0}C and 1 atm are called **standard temperature and pressure (STP).**

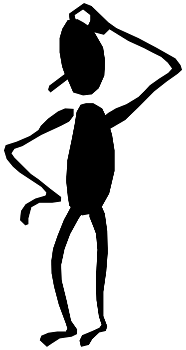
Experiments show that at STP, 1 mole of an ideal gas occupies 22.414 L.



$$PV = nRT$$

$$R = \frac{PV}{nT} = \frac{\mathbf{(1\ atm)(22.414L)}}{\mathbf{(1\ mol)(273.15\ K)}}$$

$$R = \mathbf{0.082057\ L \cdot atm\ /\ (mol \cdot K)}$$



What is the volume (in liters) occupied by 49.8 g of HCl at STP?

$$T = 0\ ^{0}\mathrm{C} = 273.15\ \mathrm{K}$$

$$P = 1\ atm$$

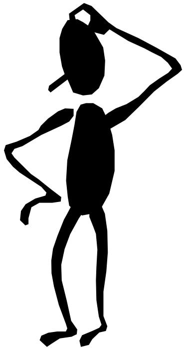
$$PV = nRT$$

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

$$n = 49.8\ \mathrm{g} \times \frac{1\ \mathrm{mol\ HCl}}{36.45\ \mathrm{g\ HCl}} = 1.37\ \mathrm{mol}$$

$$V = \frac{1.37\ \mathrm{mol} \times 0.0821 \times 273.15\ \mathrm{K}\quad \frac{\mathrm{L{\bullet}atm}}{\mathrm{mol{\bullet}K}}}{1\ \mathrm{atm}}$$

$$V = 30.6\ \mathrm{L}$$



Argon is an inert gas used in lightbulbs to retard the vaporization of the filament. A certain lightbulb containing argon at 1.20 atm and 18 ^{0}C is heated to 85 ^{0}C at constant volume. What is the final pressure of argon in the lightbulb (in atm)?

$$PV = nRT \qquad n,\ V \text{ and } R \text{ are constant}$$

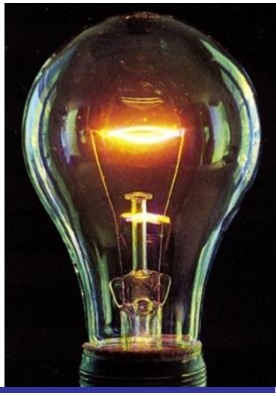
$$\frac{nR}{V} = \frac{P}{T} = \text{constant}$$

$P_1 = 1.20$ atm $\qquad P_2 = ?$

$T_1 = 291$ K $\qquad T_2 = 358$ K

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

$$P_2 = P_1 \frac{T_2}{T_1} = 1.20 \text{ atm x } \frac{358 \text{ K}}{291 \text{ K}} = 1.48 \text{ atm}$$



Densities of Gases

If we divide both sides of the ideal-gas equation by *V* and by *RT*, we get

$$PV = nRT \quad \Longrightarrow \quad \frac{n}{V} = \frac{P}{RT}$$

- We know that: moles × molecular mass = mass

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

- So multiplying both sides by the molecular mass ($\mathcal{M}$) gives

$$\frac{m}{V} = \frac{P\mathcal{M}}{RT}$$

Densities of Gases

- Mass ÷ volume = density

- So,

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

d is the density of the gas in g/L

Note: One only needs to know the molecular mass, the pressure, and the temperature to calculate the density of a gas.

We can manipulate the density equation to enable us to find the molecular mass of a gas:

$$d = \frac{PM}{RT} \Rightarrow M = \frac{dRT}{P}$$

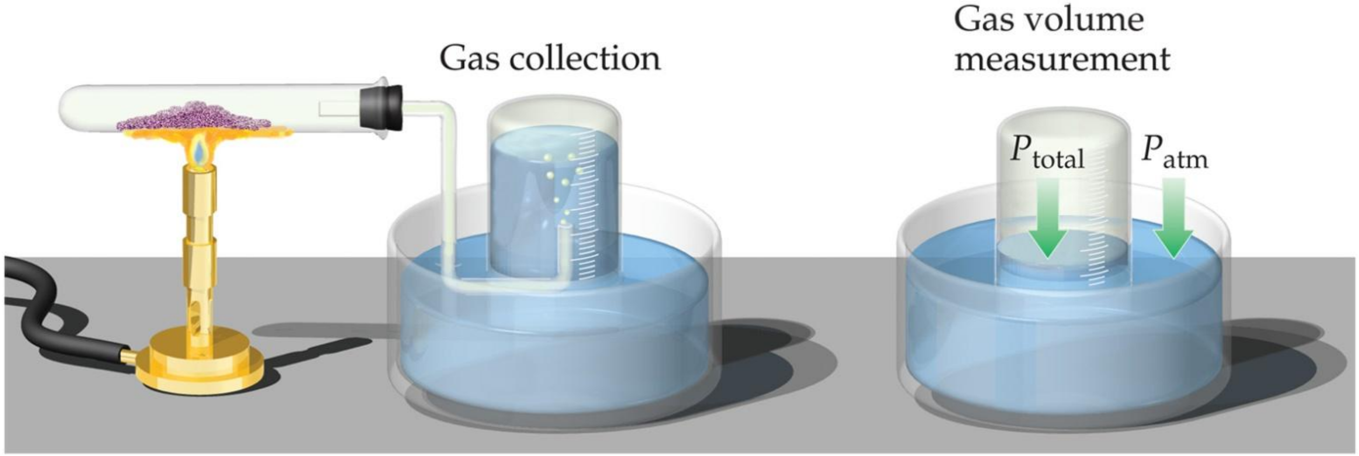
Dalton's Law of Partial Pressures

- The total pressure of a mixture of gases equals the sum of the pressures that each would exert if it were present alone.

- In other words,

$$P_{\text{total}} = P_1 + P_2 + P_3 + \ldots$$

Partial Pressures



- When one collects a gas over water, there is water vapor mixed in with the gas.

- To find only the pressure of the desired gas, one must subtract the vapor pressure of water from the total pressure.

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Sample Exercise 10.10 Applying Dalton's Law to the Partial Pressures

A gaseous mixture made from 6.00 g O_2 and 9.00 g CH_4 is placed in a 15.0-L vessel at 0 ° C. What is the partial pressure of each gas, and what is the total pressure in the vessel?

Solution

Analyze: We need to calculate the pressure for two different gases in the same volume and at the same temperature.

Plan: Because each gas behaves independently, we can use the ideal-gas equation to calculate the pressure that each would exert if the other were not present. The total pressure is the sum of these two partial pressures.

Solve: We must first convert the mass of each gas to moles:

$$n_{O_2} = (6.00\ \text{g } O_2)\left(\frac{1\ \text{mol } O_2}{32.0\ \text{g } O_2}\right) = 0.188\ \text{mol } O_2$$

$$n_{CH_4} = (9.00\ \text{g } CH_4)\left(\frac{1\ \text{mol } CH_4}{16.0\ \text{g } CH_4}\right) = 0.563\ \text{mol } CH_4$$

We can now use the ideal-gas equation to calculate the partial pressure of each gas:

$$P_{O_2} = \frac{n_{O_2}RT}{V} = \frac{(0.188\ \text{mol})(0.0821\ \text{L-atm/mol-K})(273\ \text{K})}{15.0\ \text{L}} = 0.281\ \text{atm}$$

$$P_{CH_4} = \frac{n_{CH_4}RT}{V} = \frac{(0.563\ \text{mol})(0.0821\ \text{L-atm/mol-K})(273\ \text{K})}{15.0\ \text{L}} = 0.841\ \text{atm}$$

According to Dalton's law (Equation 10.12), the total pressure in the vessel is the sum of the partial pressures:

$$P_t = P_{O_2} + P_{CH_4} = 0.281\ \text{atm} + 0.841\ \text{atm} = 1.122\ \text{atm}$$

Sample Exercise 10.10 Applying Dalton’s Law to the Partial Pressures

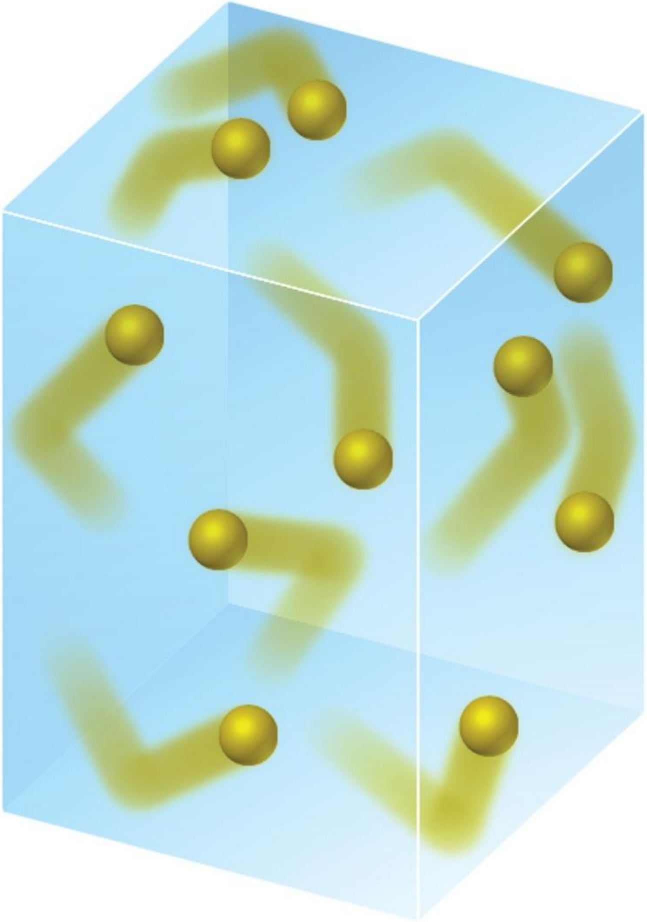
Solution (continued)

Check: Performing rough estimates is good practice, even when you may not feel that you need to do it to check an answer. In this case a pressure of roughly 1 atm seems right for a mixture of about 0.2 mol O_2 (that is, 6/32) and a bit more than 0.5 mol CH_4 (that is, 9/16), together in a 15-L volume, because one mole of an ideal gas at 1 atm pressure and 0° C occupies about 22 L.

Practice Exercise

What is the total pressure exerted by a mixture of 2.00 g of H_2 and 8.00 g of N_2 at 273 K in a 10.0-L vessel?
Answer: 2.86 atm

Kinetic-Molecular Theory



This is a model that aids in our understanding of what happens to gas particles as environmental conditions change.

Main Tenets of Kinetic-Molecular Theory

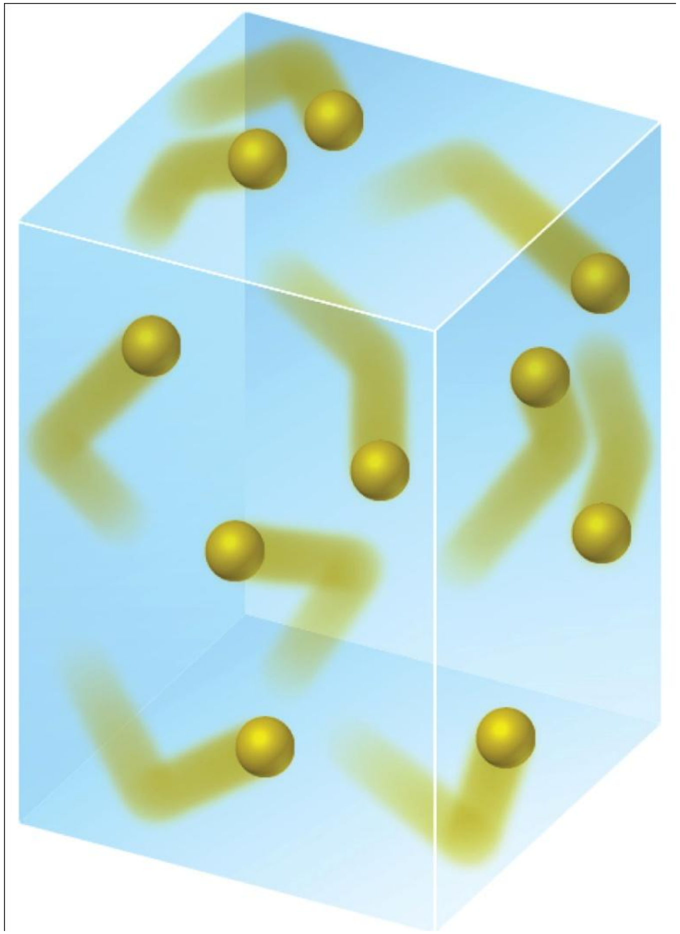
1- Gases consist of large numbers of molecules that are in continuous, random motion.

Main Tenets of Kinetic-Molecular Theory

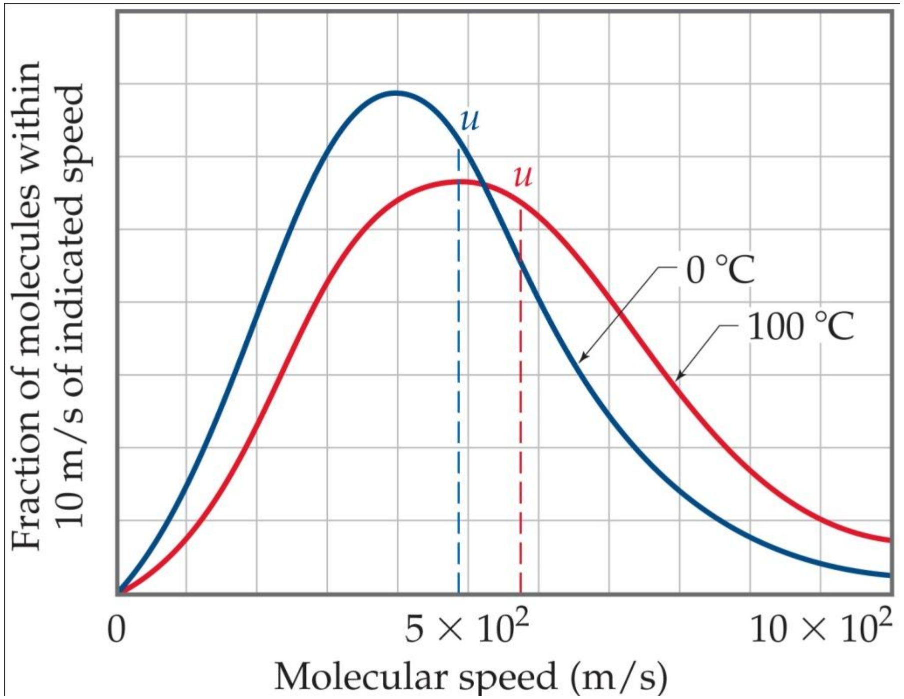
2- The combined volume of all the molecules of the gas is negligible relative to the total volume in which the gas is contained.

Main Tenets of Kinetic-Molecular Theory

3- Attractive and repulsive forces between gas molecules are negligible.



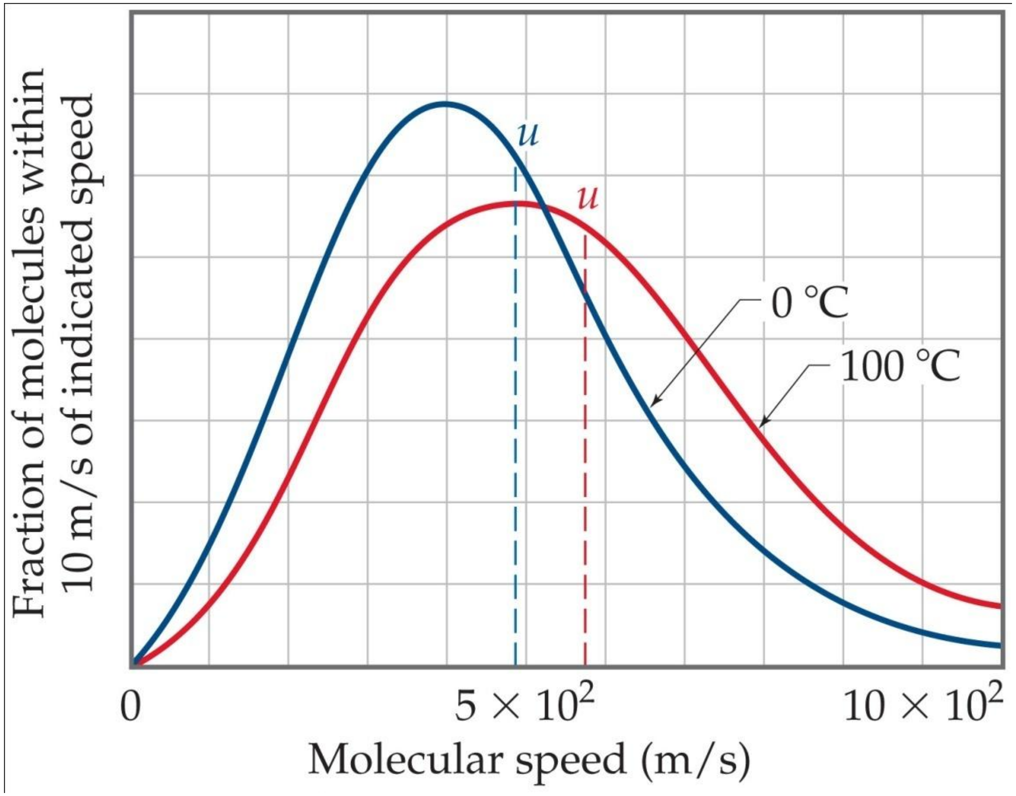
Main Tenets of Kinetic-Molecular Theory



4- Energy can be transferred between molecules during collisions, but the *average* kinetic energy of the molecules does not change with time, as long as the temperature of the gas remains constant.

Main Tenets of Kinetic-Molecular Theory

5- The average kinetic energy of the molecules is proportional to the absolute temperature.



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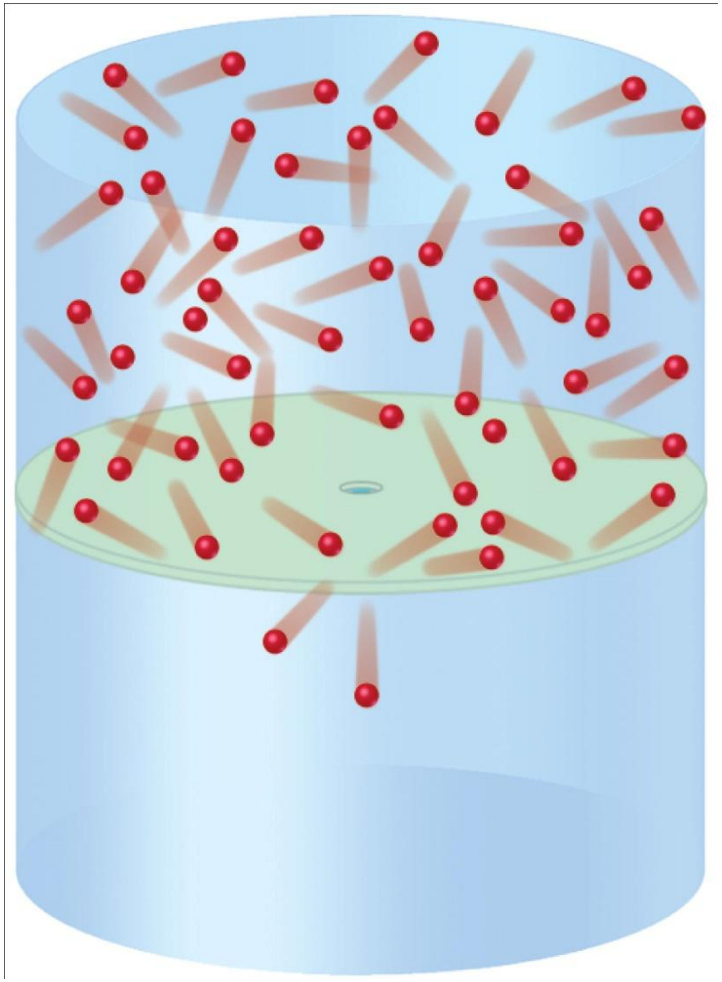
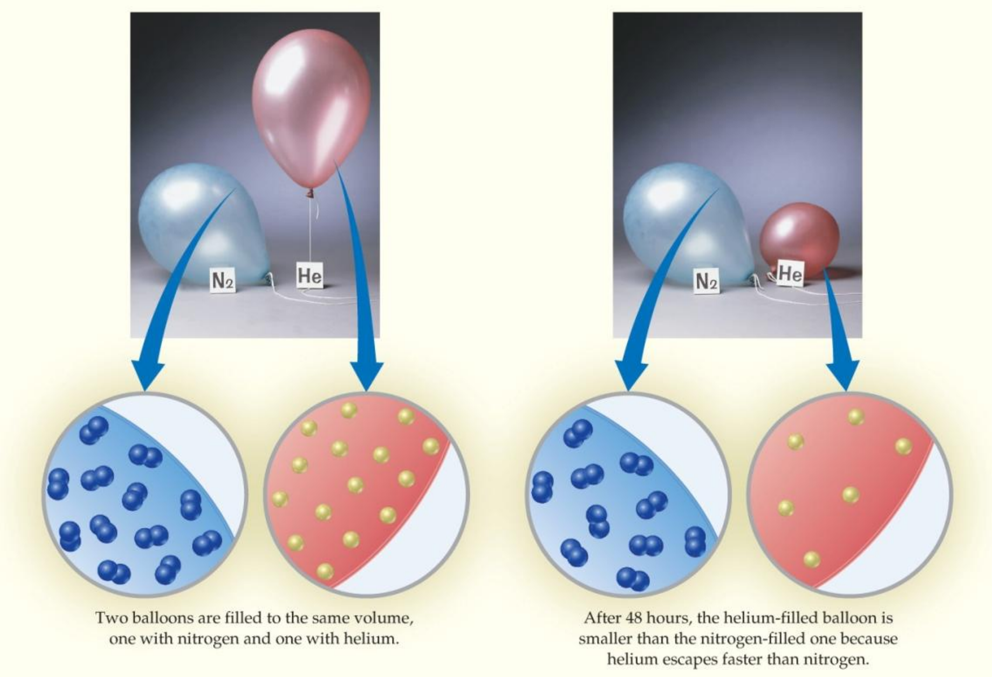
Effusion



Effusion is the escape of gas molecules through a tiny hole into an evacuated space.

Effusion

The difference in the rates of effusion for helium and nitrogen, for example, explains a helium balloon would deflate (release air or gas) faster.

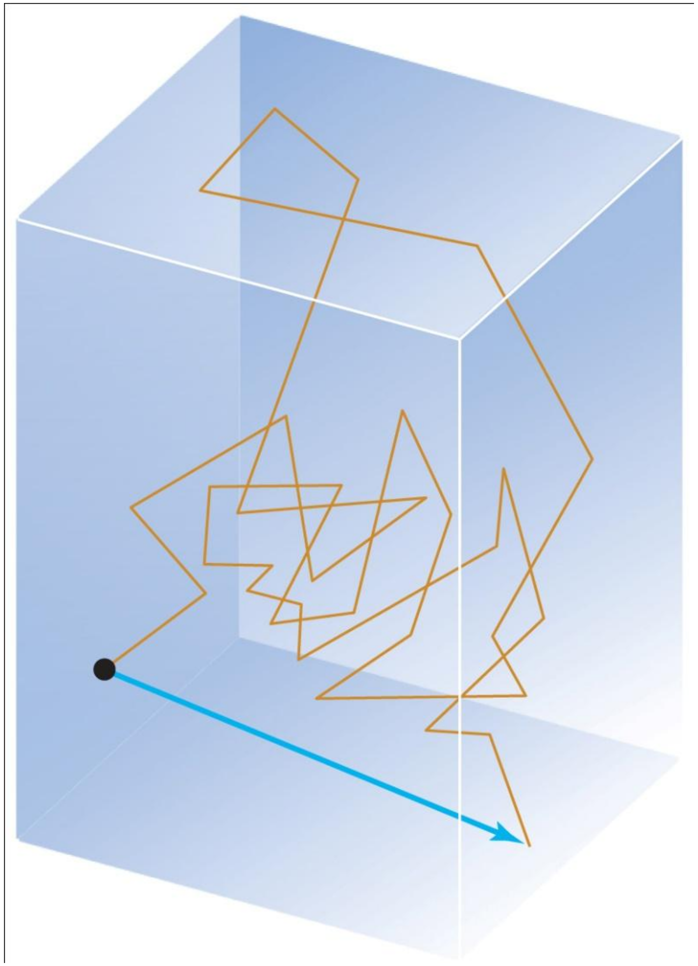


Two balloons are filled to the same volume, one with nitrogen and one with helium.

After 48 hours, the helium-filled balloon is smaller than the nitrogen-filled one because helium escapes faster than nitrogen.

Diffusion

Diffusion is the spread of one substance throughout a space or throughout a second substance.



Graham's Law

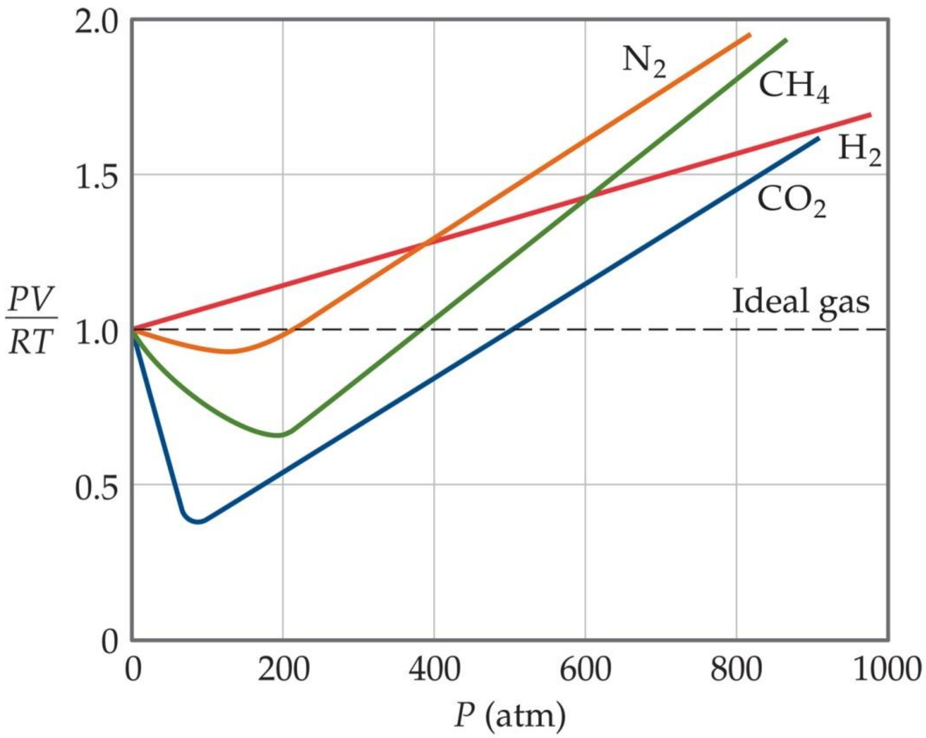
$$KE_1 = KE_2$$

$$1/2\, m_1 v_1^2 = 1/2\, m_2 v_2^2$$

$$\frac{m_1}{m_2} = \frac{v_2^2}{v_1^2}$$

$$\frac{\sqrt{\mathbf{m1}}}{\sqrt{\mathbf{m2}}} = \frac{\sqrt{v_2^2}}{\sqrt{v_1^2}} = \frac{v_2}{v_1}$$

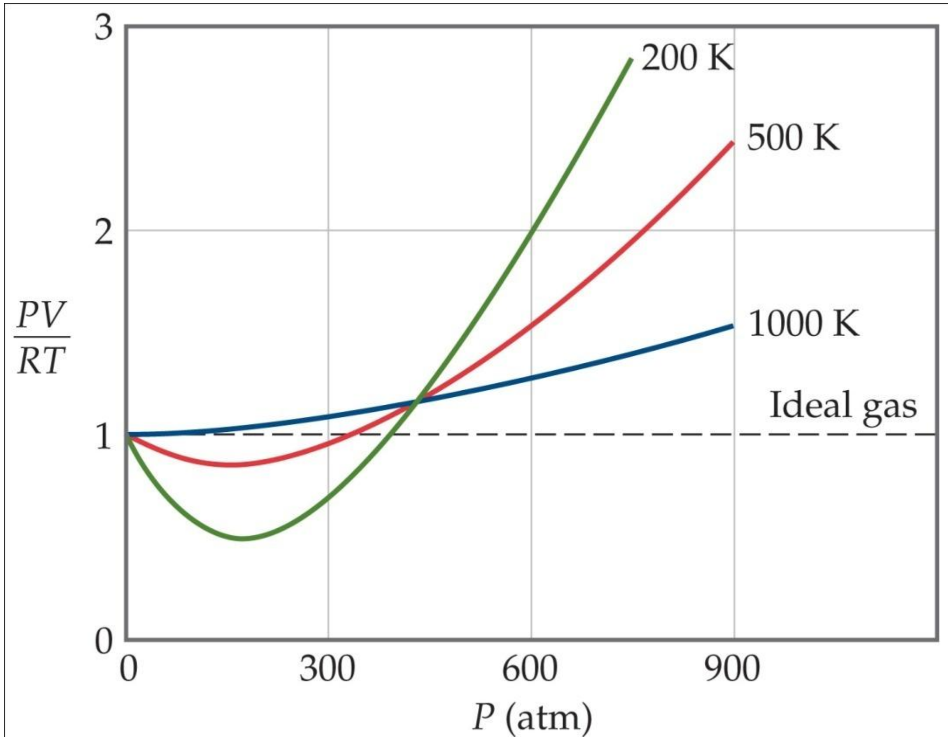
Real Gases



In the real world, the behavior of gases only conforms to the ideal-gas equation at relatively high temperature and low pressure.

Real Gases

Even the same gas will show wildly different behavior under high pressure at different temperatures.



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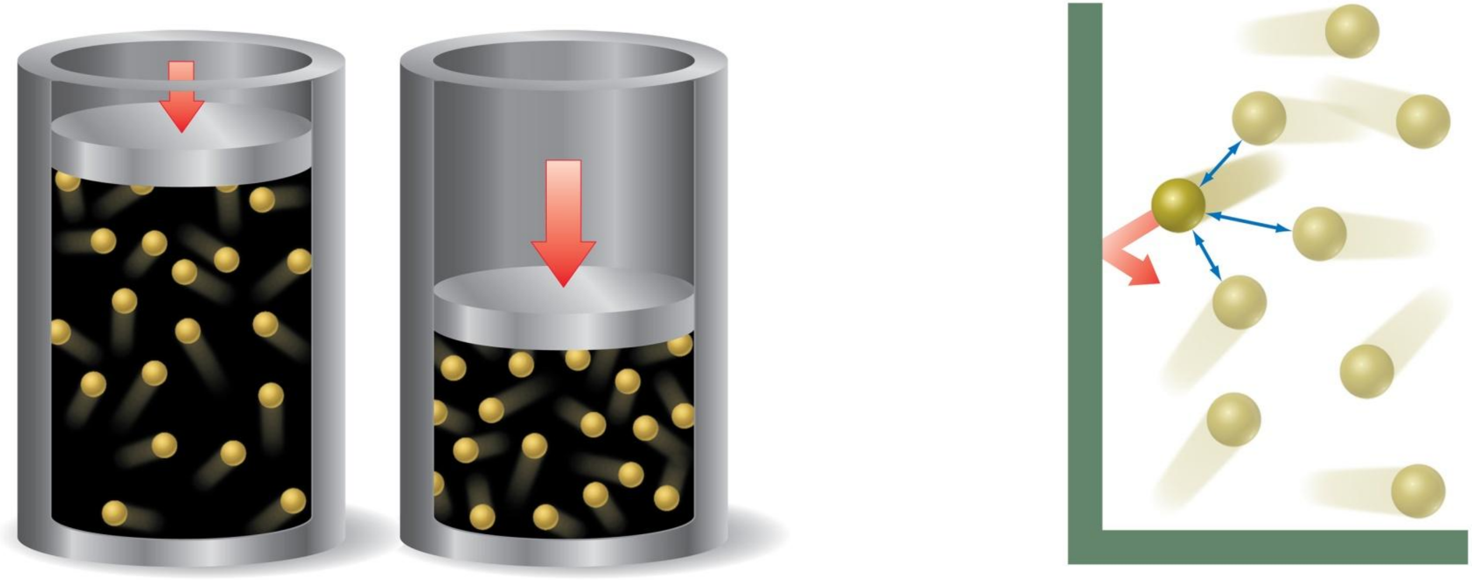
Deviations from Ideal Behavior



The assumptions made in the kinetic-molecular model (negligible volume of gas molecules themselves, no attractive forces between gas molecules, etc.) **break down** at **high pressure** and/or **low temperature**.

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Corrections for Nonideal Behavior

- The ideal-gas equation can be adjusted to take these deviations from ideal behavior into account.
- The corrected ideal-gas equation is known as the van der Waals equation.

The van der Waals Equation

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

The constants **a** and **b** have positive values and are characteristic of the individual gas. The van der Waals equation of state approaches the ideal gas law **PV=nRT** as the values of these constants approach **zero**.

The constant **a** provides a correction for the *intermolecular* forces.

Constant **b** is a correction for finite molecular **size** and its value is the *volume* of one mole of the atoms or molecules.

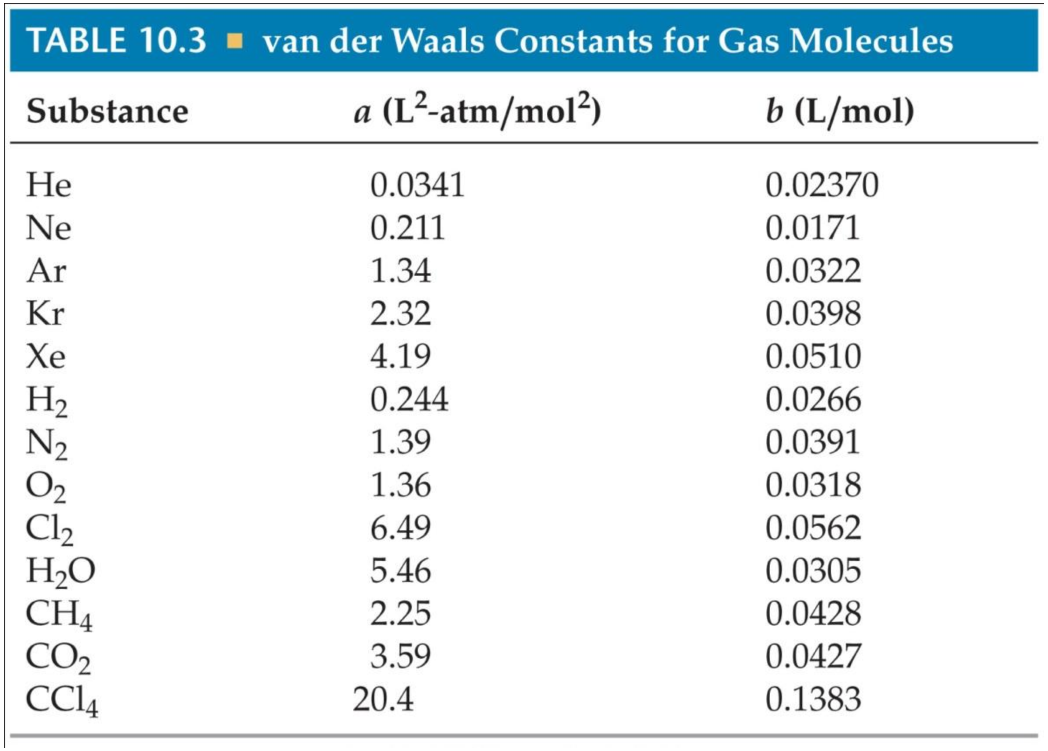
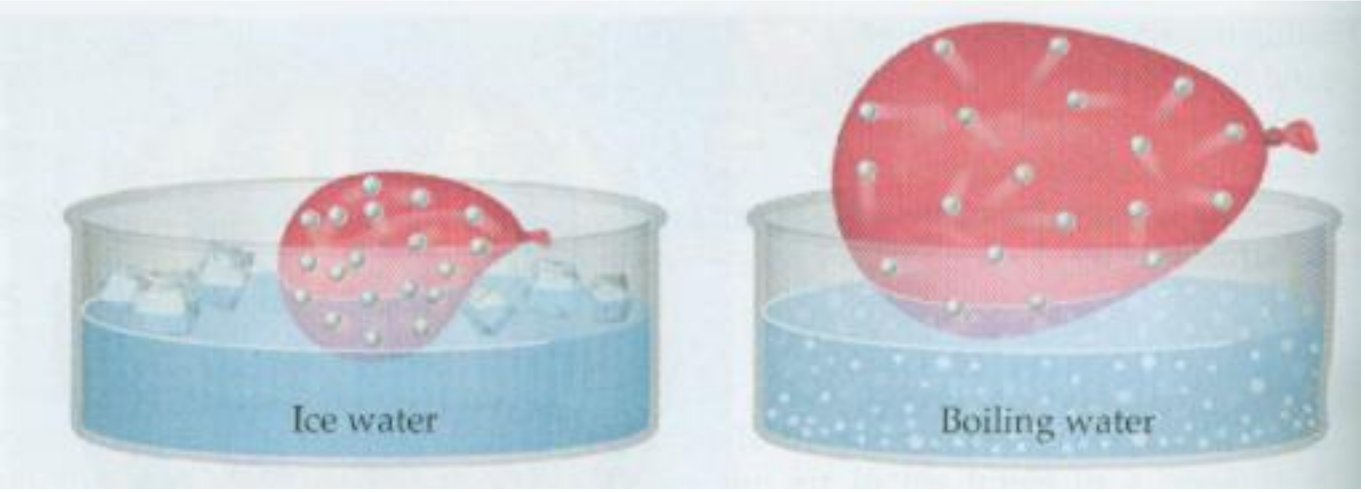


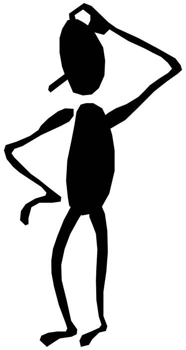
TABLE 10.3 ▪ van der Waals Constants for Gas Molecules

Substance	a (L^2-atm/mol^2)	b (L/mol)
He	0.0341	0.02370
Ne	0.211	0.0171
Ar	1.34	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0510
H_2	0.244	0.0266
N_2	1.39	0.0391
O_2	1.36	0.0318
Cl_2	6.49	0.0562
H_2O	5.46	0.0305
CH_4	2.25	0.0428
CO_2	3.59	0.0427
CCl_4	20.4	0.1383

The van der Waals constants a and b of molecular N^2 is 1.390000 and 0.039100, respectively.

Instructional examples





A sample of chlorine gas occupies a volume of 946 mL at a pressure of 726 mmHg. What is the pressure of the gas (in mmHg) if the volume is reduced at constant temperature to 154 mL?

Boyle's law

$$P \propto 1/V \longrightarrow P \times V = \text{constant}$$

$$P_1 \times V_1 = P_2 \times V_2$$

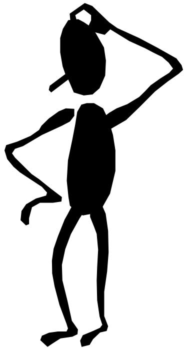
$P_1 = 726$ mmHg

$P_2 = ?$

$V_1 = 946$ mL

$V_2 = 154$ mL

$$P_2 = \frac{P_1 \times V_1}{V_2} = \frac{726 \text{ mmHg} \times 946 \cancel{\text{mL}}}{154 \cancel{\text{mL}}} = 4460 \text{ mmHg}$$



A sample of carbon monoxide gas occupies 3.20 L at 125 ^{0}C. At what temperature will the gas occupy a volume of 1.54 L if the pressure remains constant?

$$V_1/T_1 = V_2/T_2$$

$V_1 = 3.20$ L

$V_2 = 1.54$ L

$T_1 = 398.15$ K

$T_2 = ?$

$$T_2 = \frac{V_2 \text{ x } T_1}{V_1} = \frac{1.54 \cancel{\text{L}} \text{ x } 398.15 \text{ K}}{3.20 \cancel{\text{L}}} = 192 \text{ K}$$

Sample Exercise 10.4 Using the Ideal-Gas equation

Calcium carbonate, $CaCO_3(s)$, decomposes upon heating to give $CaO(s)$ and $CO_2(g)$. A sample of $CaCO_3$ is decomposed, and the carbon dioxide is collected in a 250-mL flask. After the decomposition is complete, the gas has a pressure of 1.3 atm at a temperature of 31 ° C. How many moles of CO_2 gas were generated?

Solution

Analyze: We are given the volume (250 mL), pressure (1.3 atm), and temperature 31 ° C of a sample of CO_2 gas and asked to calculate the number of moles of CO_2 in the sample.
Plan: Because we are given V, P, and T, we can solve the ideal-gas equation for the unknown quantity, n.

Solve: In analyzing and solving gas-law problems, it is helpful to tabulate the information given in the problems and then to convert the values to units that are consistent with those for R(0.0821 L-atm/mol-K). In this case the given values are

$$V = 250\text{ mL} = 0.250\text{ L}$$
$$P = 1.3\text{ atm}$$
$$T = 31\text{ °C} = (31 + 273)\text{ K} = 304\text{ K}$$

Remember: *Absolute temperature must always be used when the ideal-gas equation is solved*.

We now rearrange the ideal-gas equation (Equation 10.5) to solve for n

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

$$n = \frac{(1.3\text{ atm})\,(0.250\text{ L})}{(0.0821\text{ L-atm/mol-K})\,(304\text{ K})} = 0.013\text{ mol }CO_2$$

Check: Appropriate units cancel, thus ensuring that we have properly rearranged the ideal-gas equation and have converted to the correct units.

Sample Exercise 10.5 Calculating the Effect of Temperature Changes on Pressure

The gas pressure in an aerosol can is 1.5 atm at 25 °C. Assuming that the gas inside obeys the ideal-gas equation, what would the pressure be if the can were heated to 450 °C?

Solution

Analyze: We are given the initial pressure (1.5 atm) and temperature (25 °C) of the gas and asked for the pressure at a higher temperature (450 °C).

Plan: The volume and number of moles of gas do not change, so we must use a relationship connecting pressure and temperature. Converting temperature to the Kelvin scale and tabulating the given information, we have

	P	*T*
INITIAL	1.5 atm	298 K
FINAL	P_2	723 K

Solve: To determine how *P* and *T* are related, we start with the ideal-gas equation and isolate the quantities that do not change (*n*, *V*, and *R*) on one side and the variables (*P* and *T*) on the other side.

$$\frac{P}{T} = \frac{nR}{V} = \text{constant}$$

Because the quotient P/T is a constant, we can write

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

(where the subscripts 1 and 2 represent the initial and final states, respectively). Rearranging to solve for P_2 and substituting the given data give

$$P_2 = P_1 \times \frac{T_2}{T_1}$$

$$P_2 = (1.5\ \text{atm})\left(\frac{723\ \text{K}}{298\ \text{K}}\right) = 3.6\ \text{atm}$$

Check: This answer is intuitively reasonable—increasing the temperature of a gas increases its pressure.

Comment: It is evident from this example why aerosol cans carry a warning not to incinerate.

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Sample Exercise 10.5 Calculating the Effect of Temperature Changes on Pressure

Practice Exercise

A large natural-gas storage tank is arranged so that the pressure is maintained at 2.20 atm. On a cold day in December when the temperature is –15 ° C (4 ° F), the volume of gas in the tank is $3.25 \times 10^3\ m^3$. What is the volume of the same quantity of gas on a warm July day when the temperature is 31 ° C (88 ° F)?

Answer: $3.83 \times 10^3\ m^3$

P = 2.2 atm constant
$V1 = 3.25\ x10^3\ m^3$
V2 = ?
$T1 = -15\ C^0$
$T2 = 31\ C^0$

P = 2.2 atm constant
$V1 = 3.25\ x10^3\ m^3$
V2 = ?
T1 = -15 +273 K
T2 = 31 +273 K

$$V_1T_2 = V_2T_1$$

$$V_2 = 3.83x10^3\ m^3$$

Obtaining Other Gas Law Relationship

- **PV = nRT**

$$\frac{PV}{nT} = R$$

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

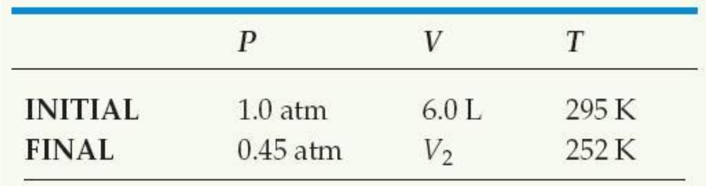
Sample Exercise 10.6 Calculating the Effect of Changing *P* and *T* on the Volume of a Gas

An inflated balloon has a volume of 6.0 L at sea level (1.0 atm) and is allowed to ascend in altitude until the pressure is 0.45 atm. During ascent the temperature of the gas falls from 22 °C to –21 °C. Calculate the volume of the balloon at its final altitude.

Solution

Analyze: We need to determine a new volume for a gas sample in a situation where both pressure and temperature change.

Plan: Let's again proceed by converting temperature to the Kelvin scale and tabulating the given information.



	P	*V*	*T*
INITIAL	1.0 atm	6.0 L	295 K
FINAL	0.45 atm	V_2	252 K

Because *n* is constant, we can use Equation 10.8.

Solve: Rearranging Equation 10.8 to solve for V_2 gives

$$V_2 = V_1 \times \frac{P_1}{P_2} \times \frac{T_2}{T_1} = (6.0\ \text{L})\left(\frac{1.0\ \text{atm}}{0.45\ \text{atm}}\right)\left(\frac{252\ \text{K}}{295\ \text{K}}\right) = 11\ \text{L}$$

Sample Exercise 10.7 Calculating Gas Density

What is the density of carbon tetrachloride vapor at 714 torr and 125 °C?

Solution

Analyze: We are asked to calculate the density of a gas given its name, its pressure, and its temperature. From the name we can write the chemical formula of the substance and determine its molar mass.
Plan: We can use Equation 10.10 to calculate the density. Before we can use that equation, however, we need to convert the given quantities to the appropriate units. We must convert temperature to the Kelvin scale and pressure to atmospheres. We must also calculate the molar mass of CCl_4.
Solve: The temperature on the Kelvin scale is 125 + 273 = 398 K.
The pressure in atmospheres is (714 torr)(1 atm/760 torr) = 0.939 atm.
The molar mass of CCl_4 is 12.0 + (4) (35.5) = 154.0 g/mol.
Using these quantities along with Equation 10.10, we have

$$d = \frac{(0.939\ \text{atm})\ (154.0\ \text{g/mol})}{(0.0821\ \text{L-atm/mol-K})\ (398\ \text{K})} = 4.43\ \text{g/L}$$

Check: If we divide the molar mass (g/mol) by the density (g/L), we end up with L/mol. The numerical value is roughly 154/4.4 = 35. That is in the right ballpark for the molar volume of a gas heated to 125 °C at near atmospheric pressure, so our answer is reasonable.

Practice Exercise

The mean molar mass of the atmosphere at the surface of Titan, Saturn's largest moon, is 28.6 g/mol. The surface temperature is 95 K, and the pressure is 1.6 atm. Assuming ideal behavior, calculate the density of Titan's atmosphere.
Answer: 5.9 g/L

Sample Exercise 10.8 Calculating the Molar Mass of a Gas

A series of measurements are made to determine the molar mass of an unknown gas. First, a large flask is evacuated and found to weigh 134.567 g. It is then filled with the gas to a pressure of 735 torr at 31 °C and reweighed. Its mass is now 137.456 g. Finally, the flask is filled with water at 31 °C and found to weigh 1067.9 g. (The density of the water at this temperature is 0.997 g/mL.) Assume that the ideal-gas equation applies, and calculate the molar mass of the unknown gas.

Solution

Analyze: We are given the temperature (31 °C) and pressure (735 torr) for a gas, together with information to determine its volume and mass, and we are asked to calculate its molar mass.

Plan: We need to use the mass information given to calculate the volume of the container and the mass of the gas within it. From this we calculate the gas density and then apply Equation 10.11 to calculate the molar mass of the gas.

Solve: The mass of the gas is the difference between the mass of the flask filled with gas and that of the empty (evacuated) flask:

$$137.456\text{ g} - 134.567\text{ g} = 2.889\text{ g}$$

The volume of the gas equals the volume of water that the flask can hold. The volume of water is calculated from its mass and density. The mass of the water is the difference between the masses of the full and empty flask:

$$1067.9\text{ g} - 134.567\text{ g} = 933.3\text{ g}$$

Sample Exercise 10.8 Calculating the Molar Mass of a Gas

Solution (continued)

By rearranging the equation for density ($d = m/V$), we have

$$V = \frac{m}{d} = \frac{(933.3\ \text{g})}{(0.997\ \text{g/mL})} = 936\ \text{mL} = 0.936\ \text{L}$$

Knowing the mass of the gas (2.889 g) and its volume (936 mL), we can calculate the density of the gas:

$$2.889\ \text{g}/0.936\ \text{L} = 3.09\ \text{g/L}$$

After converting pressure to atmospheres and temperature to kelvins, we can use Equation 10.11 to calculate the molar mass:

$$\begin{aligned}\mathcal{M} &= \frac{dRT}{P} \\ &= \frac{(3.09\ \text{g/L})(0.0821\ \text{L-atm/mol-K})(304\ \text{K})}{(735/760)\ \text{atm}} \\ &= 79.7\ \text{g/mol}\end{aligned}$$

Check: The units work out appropriately, and the value of molar mass obtained is reasonable for a substance that is gaseous near room temperature.

Practice Exercise

Calculate the average molar mass of dry air if it has a density of 1.17 g/L at 21 ° C and 740.0 torr.
Answer: 29.0 g/mol.

Sample Exercise 10.9 Relating the Volume of a Gas to the Amount of Another Substance in a Reaction

The safety air bags in automobiles are inflated by nitrogen gas generated by the rapid decomposition of sodium azide, NaN_3:

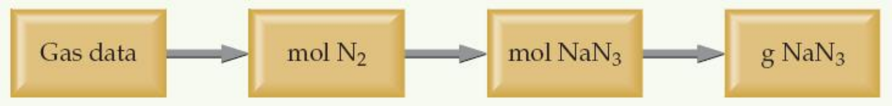
$$2\ NaN_3(s) \rightarrow 2\ Na(s) + 3\ N_2(g)$$

If an air bag has a volume of 36 L and is to be filled with nitrogen gas at a pressure of 1.15 atm at a temperature of 26.0 °C, how many grams of NaN_3 must be decomposed?

Solution

Analyze: This is a multistep problem. We are given the volume, pressure, and temperature of the N_2 gas and the chemical equation for the reaction by which the N_2 is generated. We must use this information to calculate the number of grams of NaN_3 needed to obtain the necessary N_2.

Plan: We need to use the gas data (P, V, and T) and the ideal-gas equation to calculate the number of moles of N_2 gas that should be formed for the air bag to operate correctly. We can then use the balanced equation to determine the number of moles of NaN_3. Finally, we can convert the moles of NaN_3 to grams.



Solve: The number of moles of N_2 is determined using the ideal-gas equation:

$$n = \frac{PV}{RT} = \frac{(1.15\ \text{atm})(36\ \text{L})}{(0.0821\ \text{L-atm/mol-K})(299\ \text{K})} = 1.7\ \text{mol}\ N_2$$

From here we use the coefficients in the balanced equation to calculate the number of moles of NaN_3.

$$(1.7\ \text{mol}\ N_2)\left(\frac{2\ \text{mol}\ NaN_3}{3\ \text{mol}\ N_2}\right) = 1.1\ \text{mol}\ NaN_3$$

Sample Exercise 10.9 Relating the Volume of a Gas to the Amount of Another Substance in a Reaction

Solution (continued)

Finally, using the molar mass of NaN_3, we convert moles of NaN_3 to grams:

$$(1.1 \text{ mol } NaN_3)\left(\frac{65.0 \text{ g } NaN_3}{1 \text{ mol } NaN_3}\right) = 72 \text{ g } NaN_3$$

Check: The best way to check our approach is to make sure the units cancel properly at each step in the calculation, leaving us with the correct units in the answer, g NaN_3.

Practice Exercise

In the first step in the industrial process for making nitric acid, ammonia reacts with oxygen in the presence of a suitable catalyst to form nitric oxide and water vapor:

$$4\, NH_3(g) + 5\, O_2(g) \rightarrow 4\, NO(g) + 6\, H_2O(g)$$

How many liters of $NH_3(g)$ at 850 C and 5.00 atm are required to react with 1.00 mol of $O_2(g)$ in this reaction?
Answer: 14.8 L

Sample Exercise 10.11 Relating Mole Fractions to Partial Pressures

A study of the effects of certain gases on plant growth requires a synthetic atmosphere composed of 1.5 mol percent CO_2, 18.0 mol percent O_2, and 80.5 mol percent Ar. **(a)** Calculate the partial pressure of O_2 in the mixture if the total pressure of the atmosphere is to be 745 torr. **(b)** If this atmosphere is to be held in a 121-L space at 295 K, how many moles of O_2 are needed?

Solution

Analyze: (a) We first need to calculate the partial pressure of O_2 given its mole percentage and the total pressure of the mixture.
(b) We need to calculate the number of moles of O_2 in the mixture given its volume (121 L), temperature (745 torr), and partial pressure (from part (a)).
Plan: (a) We will calculate the partial pressures using Equation 10.15. **(b)** We will then use PO_2, V, and T together with the ideal-gas equation to calculate the number of moles of O_2, n_{O_2} .

Solve: (a) The mole percent is just the mole fraction times 100. Therefore, the mole fraction of O_2 is 0.180. Using Equation 10.15, we have

$$P_{O_2} = (0.180)(745 \text{ torr}) = 134 \text{ torr}$$

$$P_{O_2} = (134 \text{ torr})\left(\frac{1 \text{ atm}}{760 \text{ torr}}\right) = 0.176 \text{ atm}$$

(b) Tabulating the given variables and changing them to appropriate units, we have

$$V = 121 \text{ L}$$

$$n_{O_2} = ?$$

$$R = 0.0821 \frac{\text{L-atm}}{\text{mol-K}}$$

$$T = 295 \text{ K}$$

Solving the ideal-gas equation for n_{O_2} , we have

$$n_{O_2} = P_{O_2}\left(\frac{V}{RT}\right)$$

$$= (0.176 \text{ atm}) \frac{121 \text{ L}}{(0.0821 \text{ L-atm/mol-K})(295 \text{ K})} = 0.879 \text{ mol}$$

Sample Exercise 10.11 Relating Mole Fractions to Partial Pressures

Solution (continued)

Check: The units check out satisfactorily, and the answer seems to be the right order of magnitude.

Practice Exercise

From data gathered by *Voyager 1*, scientists have estimated the composition of the atmosphere of Titan, Saturn's largest moon. The total pressure on the surface of Titan is 1220 torr. The atmosphere consists of 82 mol percent N_2, 12 mol percent Ar, and 6.0 mol percent CH_4. Calculate the partial pressure of each of these gases in Titan's atmosphere.
Answer: 1.0×10^3 torr N_2, 1.5×10^2 torr Ar, and 73 torr CH_4

Sample Exercise 10.12 Calculating the Amount of Gas Collected over Water

A sample of $KClO_3$ is partially decomposed (Equation 10.16), producing O_2 gas that is collected over water as in Figure 10.16. The volume of gas collected is 0.250 L at 26 °C and 765 torr total pressure. **(a)** How many moles of O_2 are collected? **(b)** How many grams of $KClO_3$ were decomposed?

Solution

(a) Analyze: We need to calculate the number of moles of O_2 gas in a container that also contains water vapor.

Plan: If we tabulate the information presented, we will see that values are given for V and T. To use the ideal-gas equation to calculate the unknown, n_{O2}, we also must know the partial pressure of O_2 in the system. We can calculate the partial pressure of O_2 from the total pressure (765 torr) and the vapor pressure of water.

Solve: The partial pressure of the O_2 gas is the difference between the total pressure, 765 torr, and the pressure of the water vapor at 26 °C, 25 torr (Appendix B):

$$P_{O_2} = 765 \text{ torr} - 25 \text{ torr} = 740 \text{ torr}$$

We can use the ideal-gas equation to calculate the number of moles of O_2:

$$n_{O_2} = \frac{P_{O_2}V}{RT} = \frac{(740 \text{ torr})(1 \text{ atm}/760 \text{ torr})(0.250 \text{ L})}{(0.0821 \text{ L-atm/mol-K})(299 \text{ K})} = 9.92 \times 10^{-3} \text{ mol } O_2$$

(b) Analyze: We now need to calculate the number of moles of reactant $KClO_3$ decomposed.

Plan: We can use the number of moles of O_2 formed and the balanced chemical equation to determine the number of moles of $KClO_3$ decomposed, which we can then convert to grams of $KClO_3$.

Solve: From Equation 10.16, we have 2 mol $KClO_3 \simeq$ 3 mol O_2. The molar mass of $KClO_3$ is 122.6 g/mol. Thus, we can convert the moles of O_2 that we found in part (a) to moles of $KClO_3$ and then to grams of $KClO_3$

Sample Exercise 10.12 Calculating the Amount of Gas Collected over Water

Solution (continued)

$$(9.92 \times 10^{-3}\ \text{mol}\ O_2)\left(\frac{2\ \text{mol}\ KClO_3}{3\ \text{mol}\ O_2}\right)\left(\frac{122.6\ \text{g}\ KClO_3}{1\ \text{mol}\ KClO_3}\right) = 0.811\ \text{g}\ KClO_3$$

Check: As always, we make sure that the units cancel appropriately in the calculations. In addition, the numbers of moles of O_2 and $KClO_3$ seem reasonable, given the small volume of gas collected.
Comment: Many chemical compounds that react with water and water vapor would be degraded by exposure to wet gas. Thus, in research laboratories gases are often dried by passing wet gas over a substance that absorbs water (a *desiccant*), such as calcium sulfate, $CaSO_4$. Calcium sulfate crystals are sold as a desiccant under the trade name Drierite™.

Practice Exercise

Ammonium nitrite, NH_4NO_2, decomposes upon heating to form N_2 gas:

$$NH_4NO_2(s) \longrightarrow N_2(g) + 2\,H_2O(l)$$

When a sample of NH_4NO_2 is decomposed in a test tube, as in Figure 10.16, 511mL of N_2 gas is collected over water at 26 ° C and 745 torr total pressure. How many grams of NH_4NO_2 were decomposed?
Answer: 1.26 g

Sample Exercise 10.13 Applying the Kinetic-Molecular Theory

A sample of O_2 gas initially at STP is compressed to a smaller volume at constant temperature. What effect does this change have on **(a)** the average kinetic energy of O_2 molecules, **(b)** the average speed of O_2 molecules, **(c)** the total number of collisions of O_2 molecules with the container walls in a unit time, **(d)** the number of collisions of O_2 molecules with a unit area of container wall per unit time?

Solution

Analyze: We need to apply the concepts of the kinetic-molecular theory to a situation in which a gas is compressed at constant temperature.

Plan: We will determine how each of the quantities in (a)–(d) is affected by the change in volume at constant temperature.

Solve: (a) The average kinetic energy of the O_2 molecules is determined only by temperature. Thus the average kinetic energy is unchanged by the compression of O_2 at constant temperature. **(b)** If the average kinetic energy of O_2 molecules does not change, the average speed remains constant. **(c)** The total number of collisions with the container walls per unit time must increase because the molecules are moving within a smaller volume but with the same average speed as before. Under these conditions they must encounter a wall more frequently. **(d)** The number of collisions with a unit area of wall per unit time increases because the total number of collisions with the walls per unit time increases and the area of the walls decreases.

Check: In a conceptual exercise of this kind, there is no numerical answer to check. All we can check in such cases is our reasoning in the course of solving the problem.

Practice Exercise

How is the rms speed of N_2 molecules in a gas sample changed by **(a)** an increase in temperature, **(b)** an increase in volume, **(c)** mixing with a sample of Ar at the same temperature?

Answer: **(a)** increases, **(b)** no effect, **(c)** no effect

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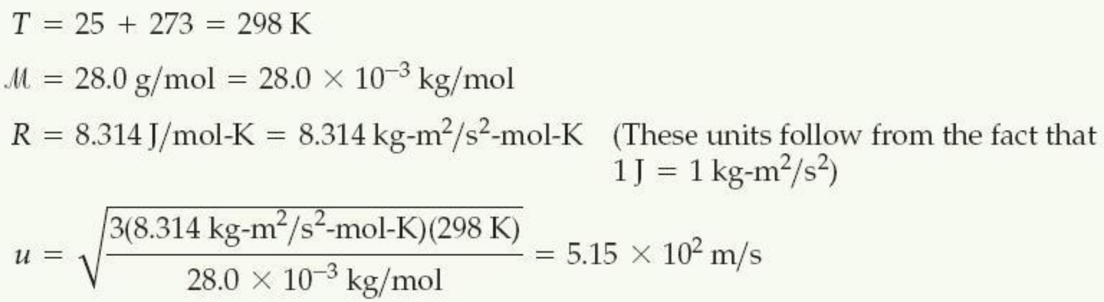
Sample Exercise 10.14 Calculating a Root-Mean-Square Speed

Calculate the rms speed, *u*, of an N_2 molecule at 25 °C.

Solution

Analyze: We are given the identity of the gas and the temperature, the two quantities we need to calculate the rms speed.
Plan: We will calculate the rms speed using Equation 10.22.
Solve: In using Equation 10.22, we should convert each quantity to SI units so that all the units are compatible. We will also use *R* in units of J/mol-K (Table 10.2) to make the units cancel correctly.



$$T = 25 + 273 = 298\ \text{K}$$

$$\mathcal{M} = 28.0\ \text{g/mol} = 28.0 \times 10^{-3}\ \text{kg/mol}$$

$$R = 8.314\ \text{J/mol-K} = 8.314\ \text{kg-m}^2/\text{s}^2\text{-mol-K} \quad \text{(These units follow from the fact that } 1\ \text{J} = 1\ \text{kg-m}^2/\text{s}^2\text{)}$$

$$u = \sqrt{\frac{3(8.314\ \text{kg-m}^2/\text{s}^2\text{-mol-K})(298\ \text{K})}{28.0 \times 10^{-3}\ \text{kg/mol}}} = 5.15 \times 10^2\ \text{m/s}$$

Comment: This corresponds to a speed of 1150 mi/hr. Because the average molecular weight of air molecules is slightly greater than that of N_2, the rms speed of air molecules is a little slower than that for N_2. The speed at which sound propagates through air is about 350 m/s, a value about two-thirds the average rms speed for air molecules.

Practice Exercise

What is the rms speed of an He atom at 25 °C?
Answer: 1.36×10^3 m/s

Sample Exercise 10.15 Applying Graham's Law

An unknown gas composed of homonuclear diatomic molecules effuses at a rate that is only 0.355 times that of O_2 at the same temperature. Calculate the molar mass of the unknown, and identify it.

Solution

Analyze: We are given the rate of effusion of an unknown gas relative to that of O_2, and we are asked to find the molar mass and identity of the unknown. Thus, we need to connect relative rates of effusion to relative molar masses.

Plan: We can use Graham's law of effusion, Equation 10.23, to determine the molar mass of the unknown gas. If we let r_x and represe$\mathcal{M}_x$he rate of effusion and molar mass of the unknown gas, Equation 10.23 can be written as follows:

$$\frac{r_x}{r_{O_2}} = \sqrt{\frac{\mathcal{M}_{O_2}}{\mathcal{M}_x}}$$

Solve: From the information given,

$$r_x = 0.355 \times r_{O_2}$$

$$\frac{r_x}{r_{O_2}} = 0.355 = \sqrt{\frac{32.0\ \text{g/mol}}{\mathcal{M}_x}}$$

Thus,

$$\frac{32.0\ \text{g/mol}}{\mathcal{M}_x} = (0.355)^2 = 0.126$$

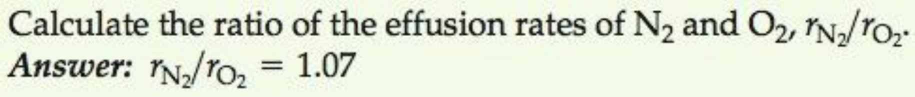
We now solve for the unknown molar mass, $\mathcal{M}_x$

$$\mathcal{M}_x = \frac{32.0\ \text{g/mol}}{0.126} = 254\ \text{g/mol}$$

Because we are told that the unknown gas is composed of homonuclear diatomic molecules, it must be an element. The molar mass must represent twice the atomic weight of the atoms in the unknown gas. We conclude that the unknown gas is I_2.

Sample Exercise 10.15 Applying Graham’s Law

Practice Exercise



Calculate the ratio of the effusion rates of N_2 and O_2, r_{N_2}/r_{O_2}.

Answer: $r_{N_2}/r_{O_2} = 1.07$

Sample Exercise 10.16 Using the van der Walls Equation

If 1.000 mol of an ideal gas were confined to 22.41 L at 0.0 °C, it would exert a pressure of 1.000 atm. Use the van der Waals equation and the constants in Table 10.3 to estimate the pressure exerted by 1.000 mol of $Cl_2(g)$ in 22.41 L at 0.0 °C.

Solution

Analyze: The quantity we need to solve for is pressure. Because we will use the van der Waals equation, we must identify the appropriate values for the constants that appear there.

Plan: Solving Equation 10.26 for P, we have

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

Solve: Substituting $n = 1.000$ mol, $R = 0.08206$ L-atm/mol-K, $T = 273.2$ K, $V = 22.41$ L, $a = 6.49$ L^2-atm/mol^2, and $b = 0.0562$ L/mol:

$$P = \frac{(1.000\ \text{mol})(0.08206\ \text{L-atm/mol-K})(273.2\ \text{K})}{22.41\ \text{L} - (1.000\ \text{mol})(0.0562\ \text{L/mol})} - \frac{(1.000\ \text{mol})^2(6.49\ \text{L}^2\text{-atm/mol}^2)}{(22.14\ \text{L})^2}$$

$$= 1.003\ \text{atm} - 0.013\ \text{atm} = 0.990\ \text{atm}$$

Check: We expect a pressure not far from 1.000 atm, which would be the value for an ideal gas, so our answer seems very reasonable.

Comment: Notice that the first term, 1.003 atm, is the pressure corrected for molecular volume. This value is higher than the ideal value, 1.000 atm, because the volume in which the molecules are free to move is smaller than the container volume, 22.41 L. Thus, the molecules must collide more frequently with the container walls. The second factor, 0.013 atm, corrects for intermolecular forces. The intermolecular attractions between molecules reduce the pressure to 0.990 atm. We can conclude, therefore, that the intermolecular attractions are the main cause of the slight deviation of $Cl_2(g)$ from ideal behavior under the stated experimental conditions.

Sample Exercise 10.16 Using the van der Walls Equation

Practice Exercise

Consider a sample of 1.000 mol of $CO_2(g)$ confined to a volume of 3.000 L at 0.0 ° C. Calculate the pressure of the gas using **(a)** the ideal-gas equation and **(b)** the van der Waals equation.
Answer: **(a)** 7.473 atm, **(b)** 7.182 atm

Sample Integrative Exercise Putting Together Concepts

Cyanogen, a highly toxic gas, is composed of 46.2% C and 53.8% N by mass. At 25 ° C and 751 torr, 1.05 g of cyanogen occupies 0.500 L. **(a)** What is the molecular formula of cyanogen? **(b)** Predict its molecular structure. **(c)** Predict the polarity of the compound.

Solution

Analyze: First we need to determine the molecular formula of a compound from elemental analysis data and data on the properties of the gaseous substance. Thus, we have two separate calculations to do.

(a) Plan: We can use the percentage composition of the compound to calculate its empirical formula. (Section 3.5) Then we can determine the molecular formula by comparing the mass of the empirical formula with the molar mass. (Section 3.5)

Solve: To determine the empirical formula, we assume that we have a 100-g sample of the compound and then calculate the number of moles of each element in the sample:

$$\text{Moles C} = (46.2\text{ g C})\left(\frac{1\text{ mol C}}{12.01\text{ g C}}\right) = 3.85\text{ mol C}$$

$$\text{Moles N} = (53.8\text{ g N})\left(\frac{1\text{ mol N}}{14.01\text{ g N}}\right) = 3.84\text{ mol N}$$

Because the ratio of the moles of the two elements is essentially 1:1, the empirical formula is CN.

To determine the molar mass of the compound, we use Equation 10.11.

$$\mathcal{M} = \frac{dRT}{p} = \frac{(1.05\text{ g}/0.500\text{ L})\,(0.0821\text{ L-atm/mol-K})\,(298\text{ K})}{(751/760)\text{ atm}} = 52.0\text{ g/mol}$$

Sample Integrative Exercise Putting Together Concepts

Solution

The molar mass associated with the empirical formula, CN, is 12.0 + 14.0 = 26.0 g/mol. Dividing the molar mass of the compound by that of its empirical formula gives (52.0 g/mol)/(26.0 g/mol) = 2.00. Thus, the molecule has twice as many atoms of each element as the empirical formula, giving the molecular formula C_2N_2.

(b) Plan: To determine the molecular structure of the molecule, we must first determine its Lewis structure. (Section 8.5) We can then use the VSEPR model to predict the structure. (Section 9.2)

Solve: The molecule has 2(4) + 2(5) = 18 valence-shell electrons. By trial and error, we seek a Lewis structure with 18 valence electrons in which each atom has an octet and in which the formal charges are as low as possible. The following structure meets these criteria:

$$:\mathrm{N}\equiv\mathrm{C}-\mathrm{C}\equiv\mathrm{N}:$$

(This structure has zero formal charge on each atom.)

The Lewis structure shows that each atom has two electron domains. (Each nitrogen has a nonbonding pair of electrons and a triple bond, whereas each carbon has a triple bond and a single bond.) Thus the electron-domain geometry around each atom is linear, causing the overall molecule to be linear.

(c) Plan: To determine the polarity of the molecule, we must examine the polarity of the individual bonds and the overall geometry of the molecule.

Solve: Because the molecule is linear, we expect the two dipoles created by the polarity in the carbon–nitrogen bond to cancel each other, leaving the molecule with no dipole moment.