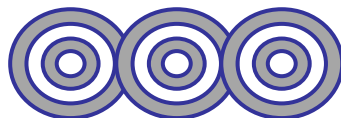




Chemistry, Raymond Chang
10th edition, 2010
McGraw-Hill



Chapter 5

Gases

Ahmad Aqel Ifseisi

Assistant Professor of Analytical Chemistry
College of Science, Department of Chemistry
King Saud University

P.O. Box 2455 Riyadh 11451 Saudi Arabia

Building: 05, Office: 2A/149 & AA/53

Tel. 014674198, Fax: 014675992

Web site: <http://fac.ksu.edu.sa/aifseisi>

E-mail: ahmad3qel@yahoo.com

aifseisi@ksu.edu.sa



كرسي أبحاث
المواد المتقدمة
Advanced Materials
Research Chair



جامعة
الملك سعود
King Saud University



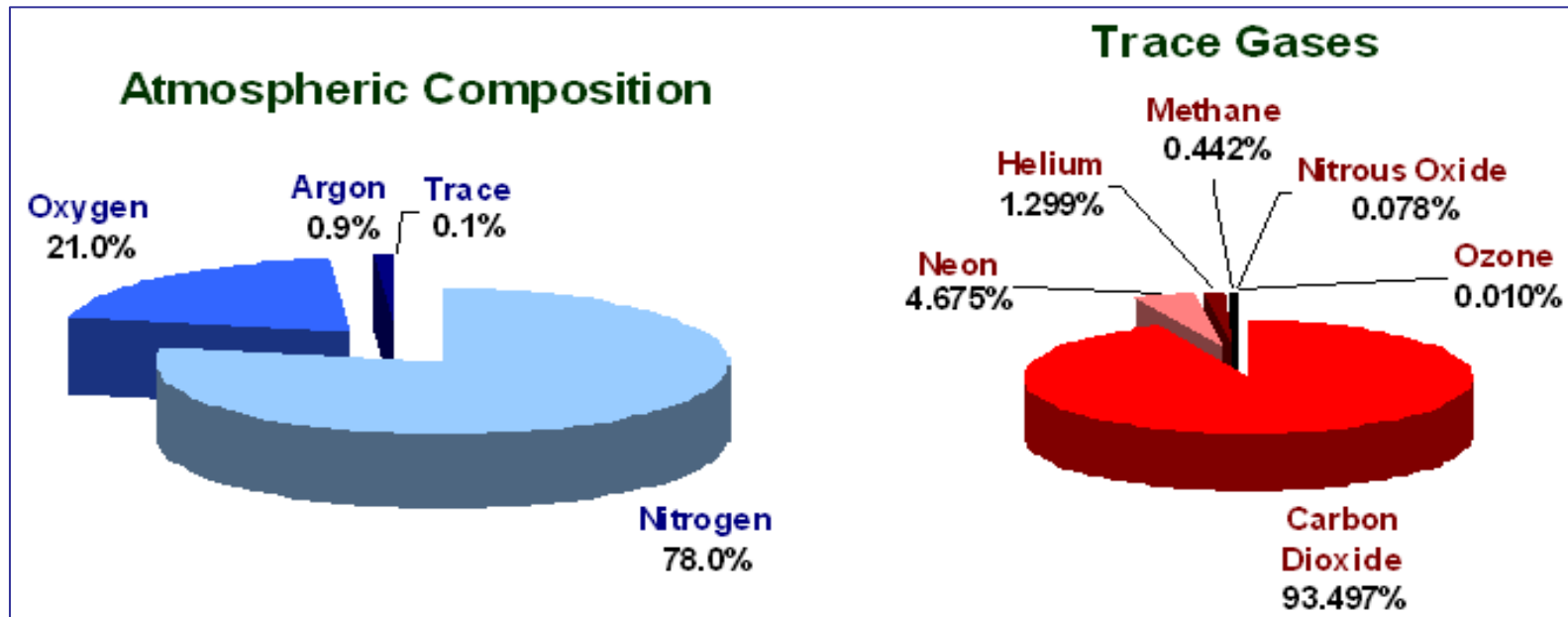
5.1

Substances that exist as gases

A **gas** is a substance that is normally in the gaseous state at ordinary temperatures and pressures.

A **vapor** is the gaseous form of any substance that is a liquid or a solid at normal temperatures and pressures.

Thus, at 25°C and 1 atm pressure, we speak of water vapor and oxygen gas.



Air is a complex mixture of several substances.

Some substances found as gases at 1 atm and 25°C

Elements

H₂ (molecular hydrogen)

N₂ (molecular nitrogen)

O₂ (molecular oxygen)

O₃ (ozone)

F₂ (molecular fluorine)

Cl₂ (molecular chlorine)

He (helium)

Ne (neon)

Ar (argon)

Kr (krypton)

Xe (xenon)

Rn (radon)

Compounds

HF (hydrogen fluoride)

HCl (hydrogen chloride)

HBr (hydrogen bromide)

HI (hydrogen iodide)

CO (carbon monoxide)

CO₂ (carbon dioxide)

NH₃ (ammonia)

NO (nitric oxide)

NO₂ (nitrogen dioxide)

N₂O (nitrous oxide)

SO₂ (sulfur dioxide)

H₂S (hydrogen sulfide)

HCN (hydrogen cyanide)*

Characteristics of gases

All gases have the following physical characteristics:

- Gases assume the volume and shape of their containers.
- Gases are the most compressible of the states of matter.
- Gases can expand spontaneously to fill their containers.
- Gases will mix evenly and completely when confined to the same container.
- Gases have much lower densities than liquids and solids.
- Gases have relatively low molar masses.

Gases form homogeneous mixtures with each other regardless of the identities or relative proportions of the component gases.

5.2

Pressure of a gas

SI Units of Pressure

Pressure is one of the most readily measurable properties of a gas.

Pressure is a force applied per unit area

$$\text{pressure} = \frac{\text{force}}{\text{area}}$$

force = mass x acceleration

The SI unit of force is the **newton (N)**, where

$$1 \text{ N} = 1 \text{ kg m/s}^2$$

The SI unit of pressure is the **pascal (Pa)**, defined as one N per m²:

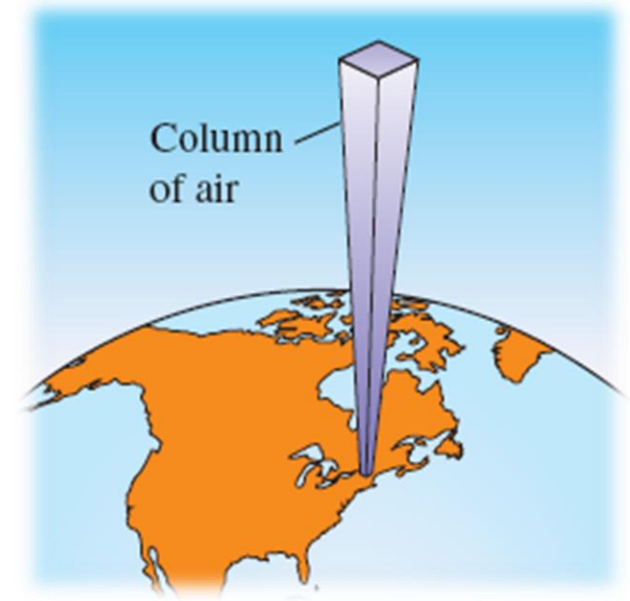
$$1 \text{ Pa} = 1 \text{ N/m}^2$$

Atmospheric Pressure

The force experienced by any area exposed to Earth's atmosphere is equal to the weight of the column of air above it.

Atmospheric pressure is the pressure exerted by Earth's atmosphere .

The actual value of atmospheric pressure depends on location, temperature, and weather conditions.



A column of air extending from sea level to the upper atmosphere.

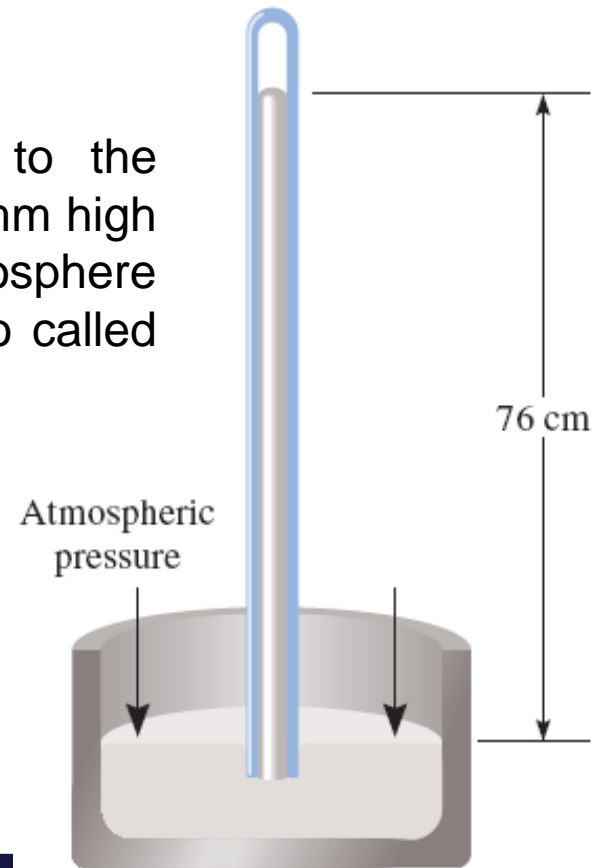
How is atmospheric pressure measured?

The **barometer** is the most familiar instrument for measuring atmospheric pressure; consists of a long glass tube, closed at one end and filled with mercury. If the tube is inverted in a dish of mercury so that no air enters the tube, some mercury will flow out of the tube into the dish, creating a vacuum at the top. The weight of the mercury remaining in the tube is supported by atmospheric pressure acting on the surface of the mercury in the dish.

Standard atmospheric pressure (1 atm) is equal to the pressure that supports a column of mercury exactly 760 mm high at 0°C at sea level. In other words, the standard atmosphere equals a pressure of 760 mmHg. The mmHg unit is also called the torr.

$$1 \text{ torr} = 1 \text{ mmHg}$$

$$1 \text{ atm} = 760 \text{ mmHg}$$



Units of Pressure

| Pressure Units | | | | | | |
|---|----------------------|---------------------------------------|-------------------------|-------------------------|---|---|
| | pascal (Pa) | bar (bar) | atmosphere (atm) | torr (torr) | pound-force per square inch (psi) | kilogram-force per square centimeter (kgf/cm ²) |
| 1 Pa | ≡ 1 N/m ² | 10 ⁻⁵ | 9.8692×10 ⁻⁶ | 7.5006×10 ⁻³ | 145.04×10 ⁻⁶ | 1.01972×10 ⁻⁵ |
| 1 bar | 100,000 | ≡ 10 ⁶ dyn/cm ² | 0.98692 | 750.06 | 14.504 | 1.01972 |
| 1 atm | 101,325 | 1.01325 | ≡ 1 atm | 760 | 14.696 | 1.03323 |
| 1 torr | 133.322 | 1.3332×10 ⁻³ | 1.3158×10 ⁻³ | ≡ 1 torr ≈ 1 mmHg | 19.337×10 ⁻³ | 1.35951×10 ⁻³ |
| 1 psi | 6,894.76 | 68.948×10 ⁻³ | 68.046×10 ⁻³ | 51.715 | ≡ 1 lbf/in ² | 7.03059×10 ⁻² |
| 1 kgf/cm² | 98,066.5 | 0.980665 | 0.967838 | 735.5576 | 14.22357 | ≡ 1 kgf/cm ² |
| Example reading: 1 Pa = 1 N/m ² = 10 ⁻⁵ bar = 9.8692×10 ⁻⁶ atm = 7.5006×10 ⁻³ torr, etc. | | | | | | |
| Note: mmHg is an abbreviation for millimetre of mercury | | | | | | |

$$1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ torr} = 1.01325 \times 10^5 \text{ Pa} = 101.325 \text{ kPa}$$

EXAMPLE

The pressure outside a jet plane flying at high altitude falls considerably below standard atmospheric pressure. Therefore, the air inside the cabin must be pressurized to protect the passengers. What is the pressure in atmospheres in the cabin if the barometer reading is 688 mmHg?

$$1 \text{ atm} = 760 \text{ mmHg},$$

$$\frac{1 \text{ atm}}{760 \text{ mmHg}}$$

$$\begin{aligned} \text{pressure} &= 688 \cancel{\text{ mmHg}} \times \frac{1 \text{ atm}}{760 \cancel{\text{ mmHg}}} \\ &= 0.905 \text{ atm} \end{aligned}$$

Practice Exercise

Convert 749 mmHg to atmospheres.

EXAMPLE

The atmospheric pressure in San Francisco on a certain day was 732 mmHg. What was the pressure in kPa?

$$1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa} = 760 \text{ mmHg}$$

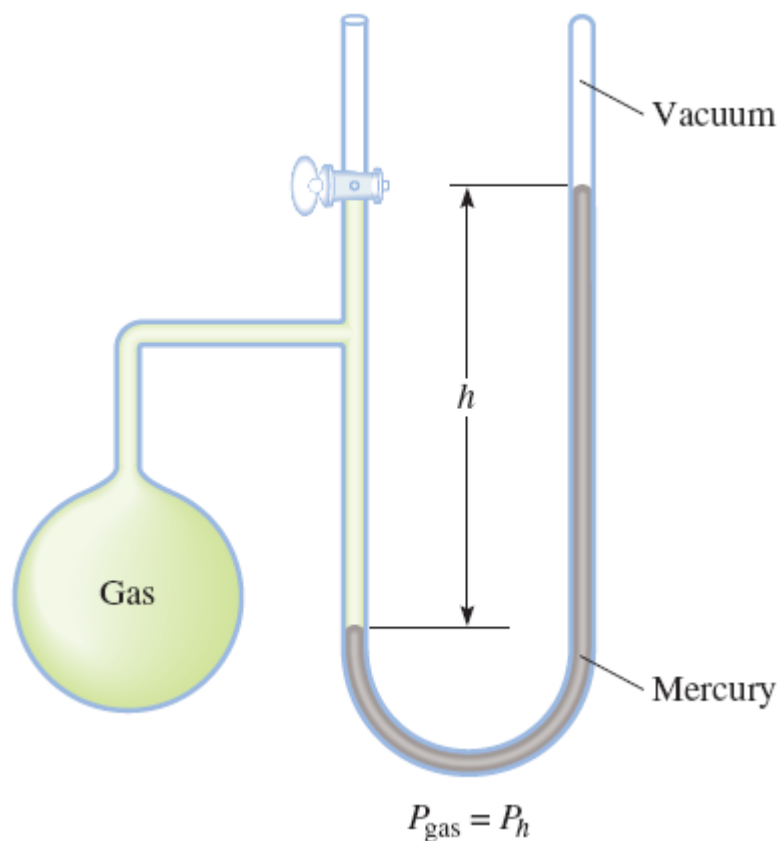
$$\frac{1.01325 \times 10^5 \text{ Pa}}{760 \text{ mmHg}}$$

$$\begin{aligned} \text{pressure} &= 732 \text{ mmHg} \times \frac{1.01325 \times 10^5 \text{ Pa}}{760 \text{ mmHg}} \\ &= 9.76 \times 10^4 \text{ Pa} \\ &= 97.6 \text{ kPa} \end{aligned}$$

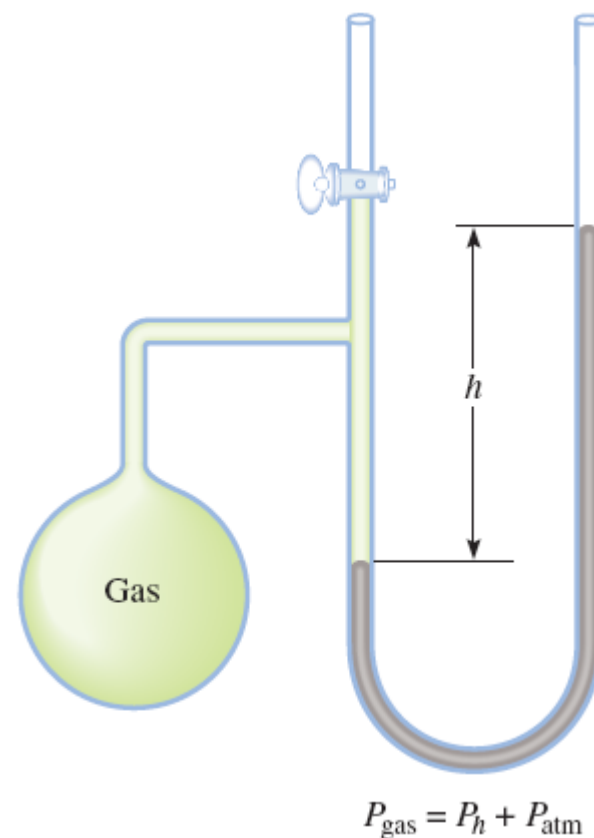
Practice Exercise

Convert 295 mmHg to kilopascals.

A *manometer* is a device used to measure the pressure of gases other than the atmosphere.



The *closed-tube manometer* is normally used to measure pressures below atmospheric pressure.



The *open-tube manometer* is better suited for measuring pressures equal to or greater than atmospheric pressure.

5.3

The gas laws

Experiments with a large number of gases reveal that four variables are needed to define the physical condition, or state of a gas:

- Temperature (**T**)
- Pressure (**P**)
- Volume (**V**)
- Amount of gas, usually expressed as the number of moles (**n**).

The equations that express the relationships among **T**, **P**, **V**, and **n** are known as the **gas laws**.

- If we want to study the relationship between **T** & **P** we should fix **V** & **n** constant.
- If we want to study the relationship between **P** & **V** we should fix **T** & **n** constant.
- and so on,,,

The Pressure-Volume Relationship: Boyle's Law

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

A mathematical expression (inverse relationship between **P** and **V**):

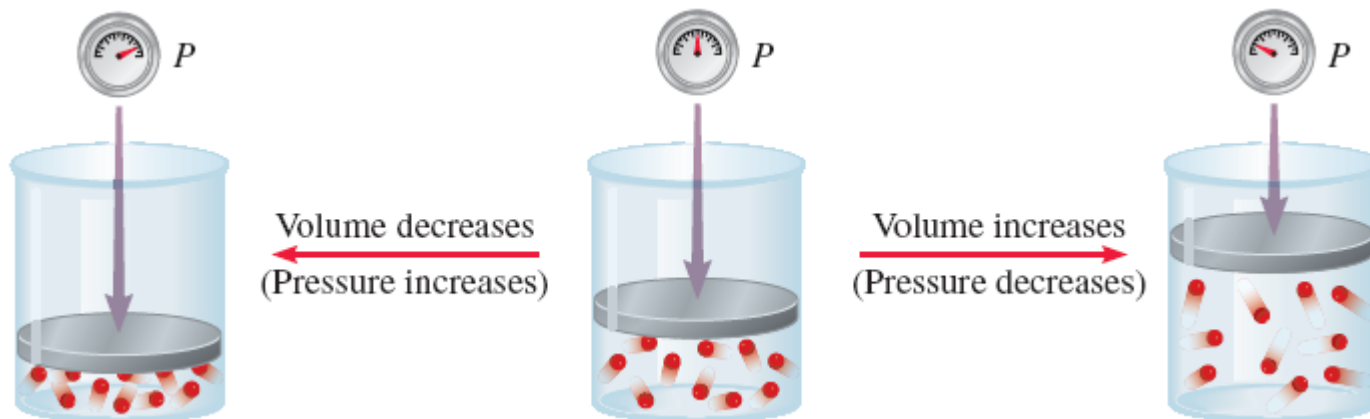
$$P \propto \frac{1}{V} \quad P = k_1 \times \frac{1}{V} \quad PV = k_1 \quad P_1V_1 = k_1 = P_2V_2$$

$P_1V_1 = P_2V_2$

where k_1 is the proportionality constant, V_1 & V_2 are the volumes at pressures P_1 & P_2 .

The product of **P** & **V** of a gas at constant **T** and amount of gas is a constant.

P times **V** is always equal to the same constant; the value of the constant depends on **T** & **n**.

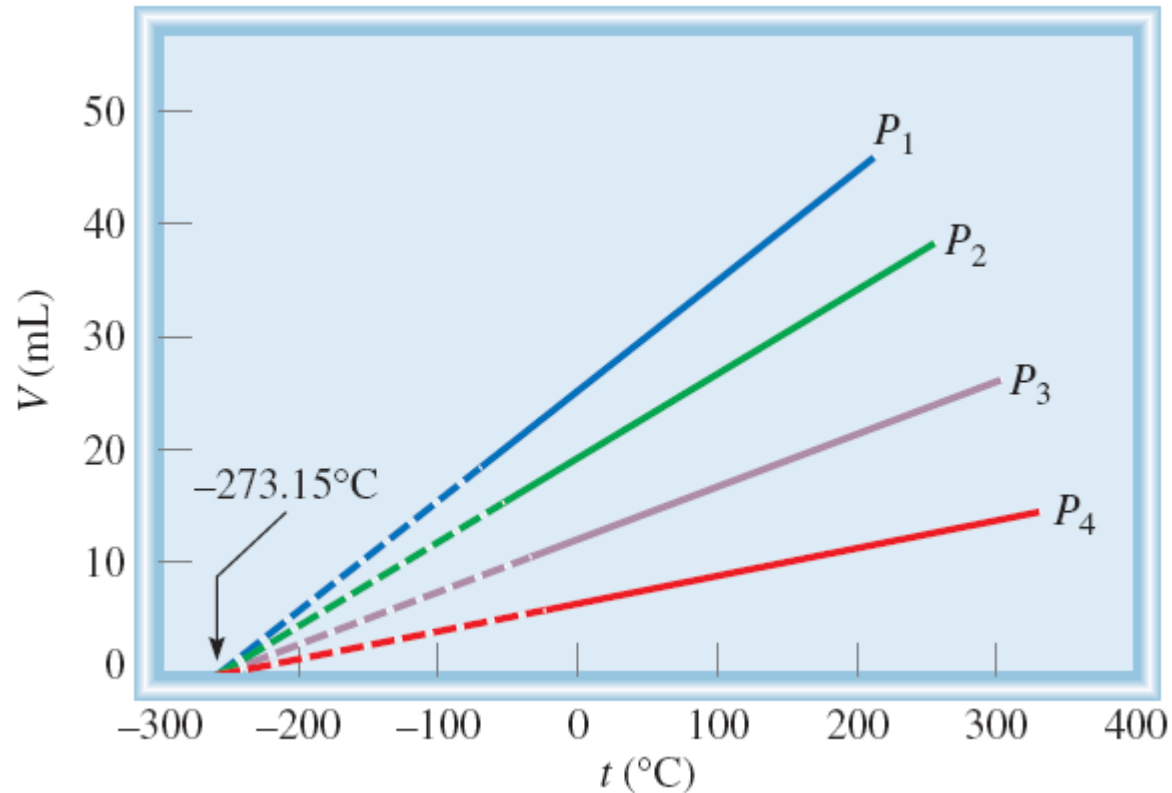


Increasing or decreasing the volume of a gas at a constant temperature.

The Temperature-Volume Relationship: Charles's and Gay-Lussac's Law

At constant pressure, the volume of a gas sample expands when heated and contracts when cooled.

At any given pressure, the plot of volume versus temperature yields a straight line. By extending the line to zero volume, we find the intercept on the temperature axis to be -273.15°C .



In 1848 Lord Kelvin identified -273.15°C as **absolute zero (0 K)**, theoretically the lowest attainable temperature. Then he set up an **absolute temperature scale**, now called the **Kelvin temperature scale**.

The volume of a fixed amount of gas maintained at constant pressure is directly proportional to the absolute temperature of the gas.

$$V \propto T$$

$$V = k_2 T$$

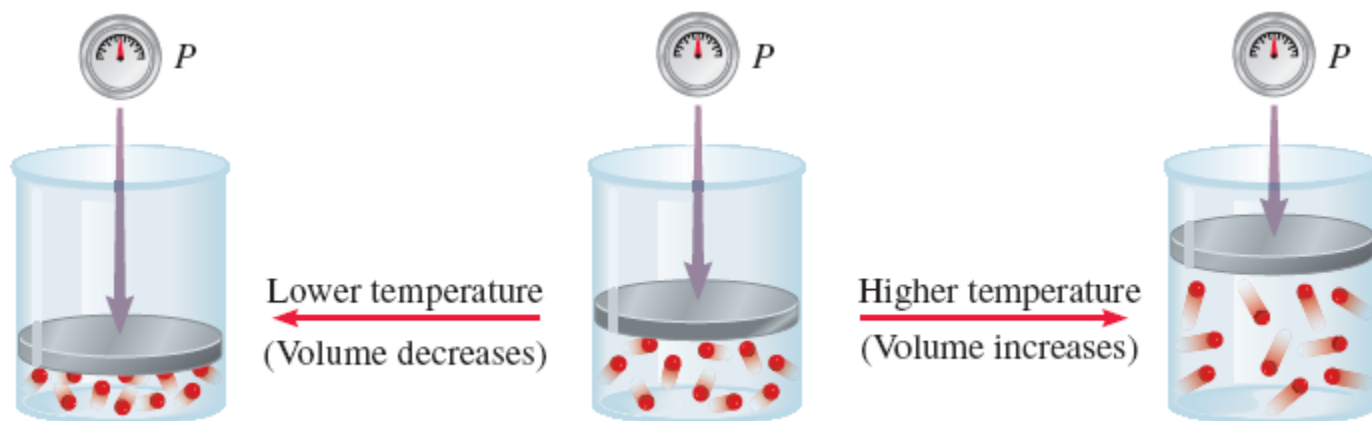
$$\frac{V}{T} = k_2$$

where k_2 is the proportionality constant. The equation is known as **Charles's and Gay-Lussac's law**, or simply **Charles's law**.

$$\frac{V_1}{T_1} = k_2 = \frac{V_2}{T_2}$$

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

where V_1 and V_2 are the volumes of the gas at temperatures T_1 and T_2 (both in kelvins), respectively.



Heating or cooling a gas at constant pressure

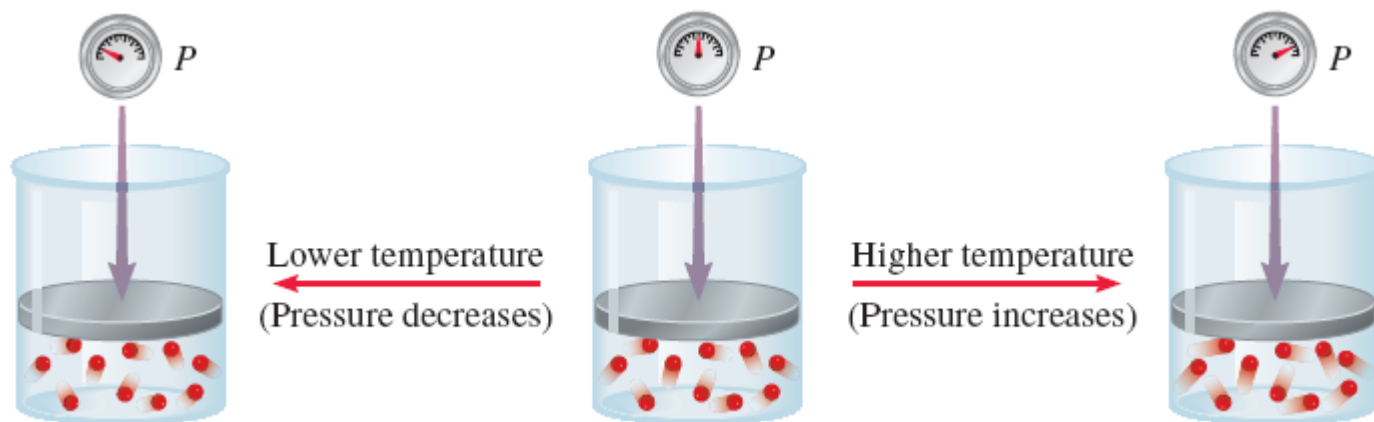
Another form of Charles's law shows that at constant amount of gas and volume, the pressure of a gas is proportional to temperature

$$P \propto T \quad P = k_3 T \quad \frac{P}{T} = k_3$$

$$\frac{P_1}{T_1} = k_3 = \frac{P_2}{T_2}$$

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

where P_1 and P_2 are the pressures of the gas at temperatures T_1 and T_2 , respectively.



Heating or cooling a gas at constant volume

The Volume-Amount Relationship: Avogadro's Law

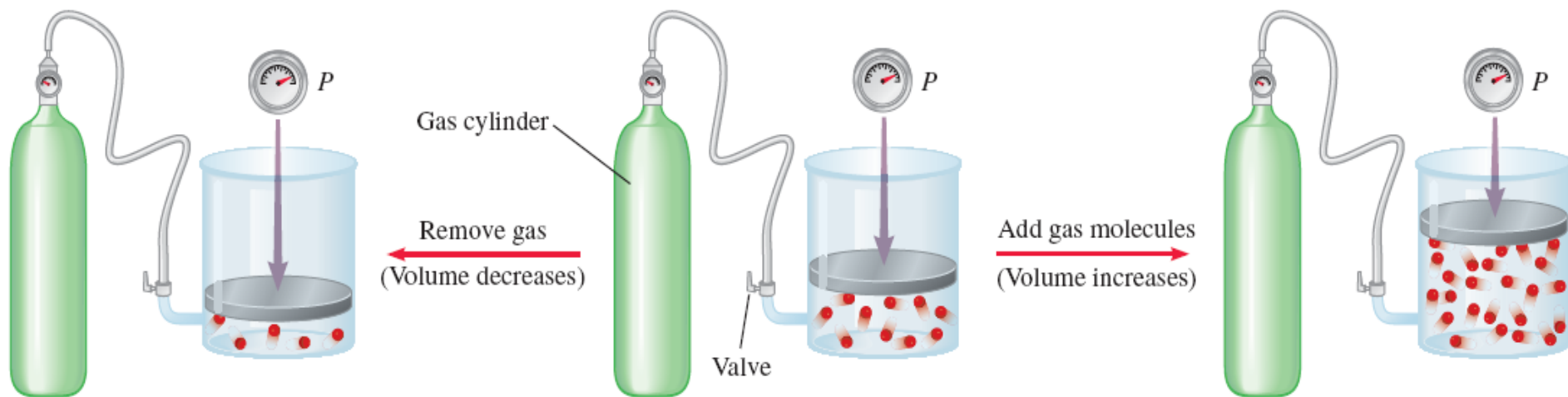
Avogadro stating that at the same **T** and **P**, equal volumes of different gases contain the same number of molecules (or atoms if the gas is monatomic).

The volume of any given gas must be proportional to the number of moles of molecules present:

$$V \propto n$$

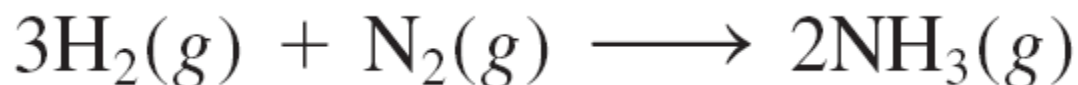
$$V = k_4 n$$

where **n** represents the number of moles, k_4 is the proportionality constant. The equation is the mathematical expression of **Avogadro's law**; states that at constant **P** & **T**, the volume of a gas is directly proportional to the number of moles of the gas present.



Dependence of volume on amount of gas at constant **T** and **P**.

According to Avogadro's law; when two gases react with each other, their reacting volumes have a simple ratio to each other. If the product is a gas, its volume is related to the volume of the reactants by a simple ratio. e.g., consider the synthesis of ammonia from molecular hydrogen and molecular nitrogen:



3 moles

1 mole

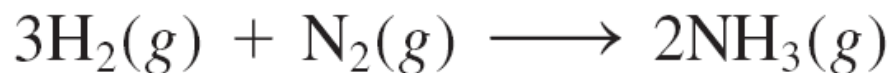
2 moles

3 molecules

1 molecule

2 molecules

Because, at the same **T** & **P**, the volumes of gases are directly proportional to the number of moles of the gases present, we can now write:



3 volumes

1 volume

2 volumes

The volume ratio of molecular hydrogen to molecular nitrogen is 3:1, and that of ammonia (the product) to the sum of the volumes of molecular hydrogen and molecular nitrogen (the reactants) is 2:4 or 1:2

5.4

The ideal gas equation

Gas laws...

Boyle's law: $V \propto \frac{1}{P}$ (at constant n and T)

Charles's law: $V \propto T$ (at constant n and P)

Avogadro's law: $V \propto n$ (at constant P and T)

We can combine all three expressions to form a single master equation for the behavior of gases:

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

$$PV = nRT$$

the *ideal gas equation*, describes the relationship among the four variables P , V , T , and n .

where **R**, the proportionality constant, is called the **gas constant**.

An **ideal gas** is a hypothetical gas whose pressure-volume-temperature behavior can be completely accounted for by the ideal gas equation.

The molecules of an ideal gas do not attract or repel one another, and their volume is negligible compared with the volume of the container.

Although there is no such thing in nature as an ideal gas, the ideal gas approximation works rather well for most reasonable T and P ranges. Thus, we can safely use the ideal gas equation to solve many gas problems.

Before we can apply the ideal gas equation to a real system, we must evaluate the gas constant R .

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

| 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

In working problems with the ideal gas equation, the units of P , T , n and V must agree with the unit in the gas constant

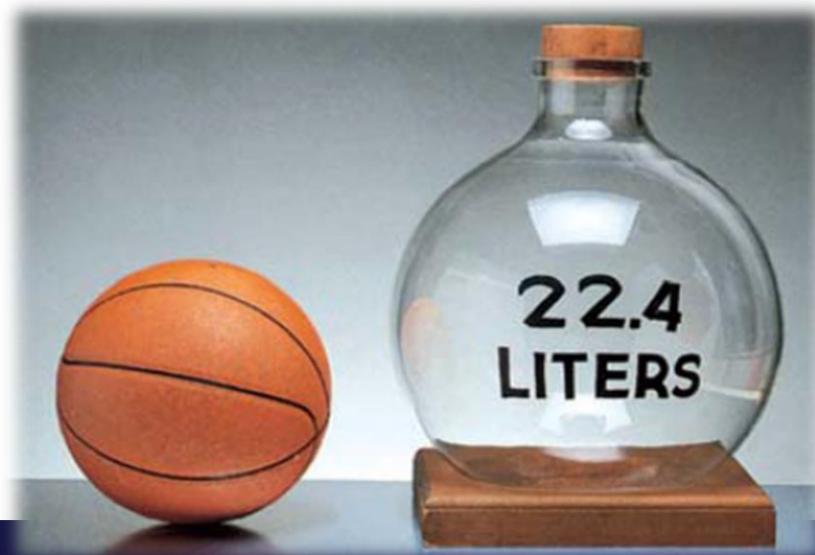
At 0°C (273.15 K) and 1 atm pressure, many real gases behave like an ideal gas. These conditions are called standard temperature and pressure (**STP**).

Suppose you have 1.00 mol of an ideal gas at **STP**. According to the ideal gas equation, the volume of the gas is:

$$V = \frac{nRT}{P} = \frac{(1.000 \text{ mol})(0.08206 \text{ L-atm/mol-K})(273.15 \text{ K})}{1.000 \text{ atm}} = 22.41 \text{ L}$$

The volume occupied by one mole of ideal gas at **STP** (22.41 L) is known as the **molar volume** of an ideal gas at **STP**.

1 mole of an ideal gas occupies 22.414 L, which is somewhat greater than the volume of a basketball.



EXAMPLE

Sulfur hexafluoride (SF_6) is a colorless, odorless, very unreactive gas. Calculate the pressure (in atm) exerted by 1.82 moles of the gas in a steel vessel of volume 5.43 L at 69.5°C .

$$\begin{aligned} P &= \frac{nRT}{V} \\ &= \frac{(1.82 \text{ mol})(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(69.5 + 273) \text{ K}}{5.43 \text{ L}} \\ &= 9.42 \text{ atm} \end{aligned}$$

Practice Exercise

Calculate the volume (in liters) occupied by 2.12 moles of nitric oxide (NO) at 6.54 atm and 76°C .

EXAMPLE

Calculate the volume (in liters) occupied by 7.40 g of NH_3 at STP.

$$n = 7.4 / 17.03 = 0.4345 \text{ mol}$$

$$V = \frac{nRT}{P} = (0.4345 \times 0.0821 \times 273) / 1 = 9.74 \text{ L}$$

By using the fact that the molar volume of a gas occupies 22.41 L at STP, we can calculate the volume of a gas at STP without using the ideal gas equation.

$$V = 7.40 \text{ g NH}_3 \times \frac{1 \text{ mol NH}_3}{17.03 \text{ g NH}_3} \times \frac{22.41 \text{ L}}{1 \text{ mol NH}_3}$$
$$= 9.74 \text{ L}$$

Practice Exercise

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

If we need to deal with changes in pressure, volume, temperature, or the amount of gas, we must employ a modified form of the ideal gas equation that takes into account the initial and final conditions.

$$R = \frac{P_1 V_1}{n_1 T_1} \text{ (before change)}$$

$$R = \frac{P_2 V_2}{n_2 T_2} \text{ (after change)}$$

$$\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}$$

If $n_1 = n_2$, as is usually the case because the amount of gas normally does not change, the equation then becomes

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

The subscripts 1 and 2 denote the initial and final states of the gas, respectively.

EXAMPLE

An inflated helium balloon with a volume of 0.55 L at sea level (1.0 atm) is allowed to rise to a height of 6.5 km, where the pressure is about 0.40 atm. Assuming that the temperature remains constant, what is the final volume of the balloon?

$$\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}$$

Because $n_1 = n_2$ and $T_1 = T_2$,

$$P_1 V_1 = P_2 V_2$$

| Initial Conditions | Final Conditions |
|-------------------------|--------------------------|
| $P_1 = 1.0 \text{ atm}$ | $P_2 = 0.40 \text{ atm}$ |
| $V_1 = 0.55 \text{ L}$ | $V_2 = ?$ |

Therefore,

$$\begin{aligned} V_2 &= V_1 \times \frac{P_1}{P_2} \\ &= 0.55 \text{ L} \times \frac{1.0 \text{ atm}}{0.40 \text{ atm}} \\ &= 1.4 \text{ L} \end{aligned}$$

As pressure decreased, volume increased

Practice Exercise

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

EXAMPLE

Argon is an inert gas used in lightbulbs to retard the vaporization of the tungsten filament. A certain lightbulb containing argon at 1.20 atm and 18°C is heated to 85°C at constant volume. Calculate its final pressure (in atm).

Because $n_1 = n_2$ and $V_1 = V_2$, the Equation becomes

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

| Initial Conditions | Final Conditions |
|--|--|
| $P_1 = 1.20 \text{ atm}$ | $P_2 = ?$ |
| $T_1 = (18 + 273) \text{ K} = 291 \text{ K}$ | $T_2 = (85 + 273) \text{ K} = 358 \text{ K}$ |

$$\begin{aligned} P_2 &= P_1 \times \frac{T_2}{T_1} \\ &= 1.20 \text{ atm} \times \frac{358 \text{ K}}{291 \text{ K}} \\ &= 1.48 \text{ atm} \end{aligned}$$

Practice Exercise

A sample of oxygen gas initially at 0.97 atm is cooled from 21°C to -68°C at constant volume. What is its final pressure (in atm)?

EXAMPLE

A small bubble rises from the bottom of a lake, where the T and P are 8°C and 6.4 atm , to the water's surface, where the temperature is 25°C and the pressure is 1.0 atm . Calculate the final volume (in mL) of the bubble if its initial volume was 2.1 mL .

$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$ the amount of air in the bubble remains constant, that is,
 $n_1 = n_2$ so that

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

| Initial Conditions | Final Conditions |
|---|--|
| $P_1 = 6.4\text{ atm}$ | $P_2 = 1.0\text{ atm}$ |
| $V_1 = 2.1\text{ mL}$ | $V_2 = ?$ |
| $T_1 = (8 + 273)\text{ K} = 281\text{ K}$ | $T_2 = (25 + 273)\text{ K} = 298\text{ K}$ |

$$\begin{aligned}V_2 &= V_1 \times \frac{P_1}{P_2} \times \frac{T_2}{T_1} \\&= 2.1\text{ mL} \times \frac{6.4\text{ atm}}{1.0\text{ atm}} \times \frac{298\text{ K}}{281\text{ K}} \\&= 14\text{ mL}\end{aligned}$$

Practice Exercise

A gas initially at 4.0 L , 1.2 atm , and 66°C undergoes a change so that its final volume and temperature are 1.7 L and 42°C . What is its final pressure? Assume the number of moles remains unchanged.

Density Calculations

If we rearrange the ideal gas equation, we can calculate the density of a gas:

$$PV = nRT \longrightarrow \frac{n}{V} = \frac{P}{RT} \xrightarrow[\substack{n = \frac{m}{\mathcal{M}} \\ d = \frac{m}{V}}]{d = \frac{P \mathcal{M}}{RT}}$$

Unlike molecules in condensed matter (that is, in liquids and solids), gaseous molecules are separated by distances that are large compared with their size.

Consequently, the density of gases is very low under atmospheric conditions. For this reason, gas densities are usually expressed in (g/L) rather than (g/mL).

EXAMPLE

Calculate the density of carbon dioxide (CO_2) in grams per liter (g/L) at 0.990 atm and 55°C .

$$T = 273 + 55 = 328 \text{ K}$$

$$\begin{aligned} d &= \frac{PM}{RT} \\ &= \frac{(0.990 \text{ atm})(44.01 \text{ g/mol})}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(328 \text{ K})} = 1.62 \text{ g/L} \end{aligned}$$

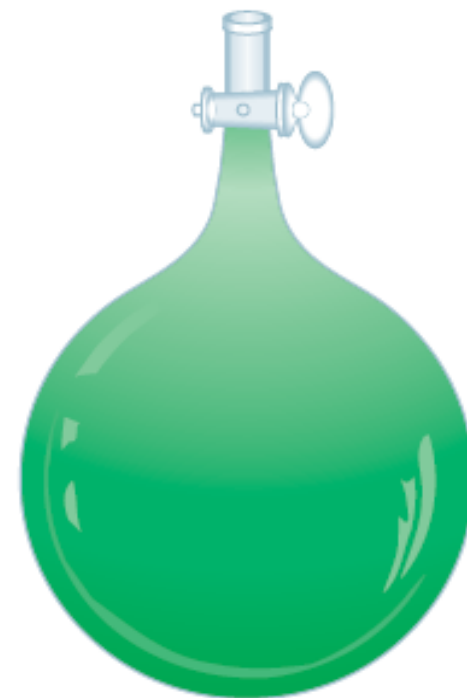
Practice Exercise

What is the density (in g/L) of uranium hexafluoride (UF_6) at 779 mmHg and 62°C ?

The Molar Mass of a Gaseous Substance

$$d = \frac{P \mathcal{M}}{RT} \longrightarrow \mathcal{M} = \frac{dRT}{P}$$

A **bulb** of known volume is filled with the gas under study at a certain T and P . First the bulb is weighed, and then it is emptied (evacuated) and weighed again. The difference in masses gives the mass of the gas. Knowing the volume of the bulb, we can calculate the density of the gas. Once we know the density of a gas, we can calculate the molar mass of the substance.



An apparatus for measuring the density of a gas

EXAMPLE

A chemist has synthesized a greenish-yellow gaseous compound of chlorine and oxygen and finds that its density is 7.71 g/L at 36°C and 2.88 atm. Calculate the molar mass of the compound and determine its molecular formula.

$$\begin{aligned}\mathcal{M} &= \frac{dRT}{P} \\ &= \frac{(7.71 \text{ g/L})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(36 + 273) \text{ K}}{2.88 \text{ atm}} \\ &= 67.9 \text{ g/mol}\end{aligned}$$

Alternatively,

$$\text{molar mass of compound} = \frac{\text{mass of compound}}{\text{moles of compound}}$$

$$\begin{aligned}n &= \frac{PV}{RT} \\ &= \frac{(2.88 \text{ atm})(1.00 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(309 \text{ K})} \\ &= 0.1135 \text{ mol}\end{aligned}$$

$$\mathcal{M} = \frac{\text{mass}}{\text{number of moles}} = \frac{7.71 \text{ g}}{0.1135 \text{ mol}} = 67.9 \text{ g/mol}$$

the compound must contain one Cl atom and two O atoms and have the formula ClO_2 , which has a molar mass of 67.45 g.

EXAMPLE

Chemical analysis of a gaseous compound showed that it contained 33.0 percent silicon (Si) and 67.0 percent fluorine (F) by mass. At 35°C, 0.210 L of the compound exerted a pressure of 1.70 atm. If the mass of 0.210 L of the compound was 2.38 g, calculate the molecular formula of the compound.

By assuming that we have 100 g of the compound, so the percentages are converted to grams. The number of moles of Si and F are:

$$n_{\text{Si}} = 33.0 \text{ g Si} \times \frac{1 \text{ mol Si}}{28.09 \text{ g Si}} = 1.17 \text{ mol Si}$$
$$n_{\text{F}} = 67.0 \text{ g F} \times \frac{1 \text{ mol F}}{19.00 \text{ g F}} = 3.53 \text{ mol F}$$

The empirical formula is $\text{Si}_{1.17}\text{F}_{3.53}$, dividing by the smaller subscript (1.17), we obtain SiF_3 .

$$n = \frac{PV}{RT}$$
$$= \frac{(1.70 \text{ atm})(0.210 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(308 \text{ K})} = 0.0141 \text{ mol}$$

$$\mathcal{M} = \frac{2.38 \text{ g}}{0.0141 \text{ mol}} = 169 \text{ g/mol}$$

The molar mass of the empirical formula SiF_3 is 85.09 g.

The ratio (molar mass/empirical molar mass) is always an integer ($169/85.09 \sim 2$).

Therefore, the molecular formula of the compound must be $(\text{SiF}_3)_2$ or Si_2F_6 .

Practice Exercise

The density of a gaseous organic compound is 3.38 g/L at 40°C and 1.97 atm. What is its molar mass?

Practice Exercise

A gaseous compound is 78.14 percent boron and 21.86 percent hydrogen. At 27°C, 74.3 mL of the gas exerted a pressure of 1.12 atm. If the mass of the gas was 0.0934 g, what is its molecular formula?

5.5

Gas stoichiometry

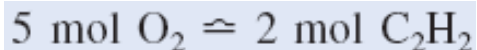
EXAMPLE

Calculate the volume of O₂ (in liters) required for the complete combustion of 7.64 L of acetylene (C₂H₂) measured at the same temperature and pressure.

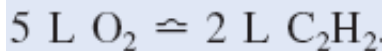


According to Avogadro's law, at the same T and P , the number of moles of gases are directly related to their volumes.

From the equation,



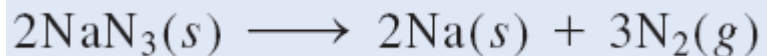
Therefore, we can also write



$$\begin{aligned} \text{volume of O}_2 &= 7.64 \text{ L C}_2\text{H}_2 \times \frac{5 \text{ L O}_2}{2 \text{ L C}_2\text{H}_2} \\ &= 19.1 \text{ L} \end{aligned}$$

EXAMPLE

Sodium azide (NaN_3) is used in some automobile air bags. The impact of a collision triggers the decomposition of NaN_3 as follows:



The nitrogen gas produced quickly inflates the bag between the driver and the windshield and dashboard. Calculate the volume of N_2 generated at 80°C and 823 mmHg by the decomposition of 60.0 g of NaN_3 .

$$2 \text{ mol NaN}_3 \approx 3 \text{ mol N}_2$$

$$\frac{3 \text{ mol N}_2}{2 \text{ mol NaN}_3}$$

$$\begin{aligned} \text{moles of N}_2 &= 60.0 \text{ g NaN}_3 \times \frac{1 \text{ mol NaN}_3}{65.02 \text{ g NaN}_3} \times \frac{3 \text{ mol N}_2}{2 \text{ mol NaN}_3} \\ &= 1.38 \text{ mol N}_2 \end{aligned}$$

$$\begin{aligned} V &= \frac{nRT}{P} = \frac{(1.38 \text{ mol})(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(80 + 273 \text{ K})}{(823/760) \text{ atm}} \\ &= 36.9 \text{ L} \end{aligned}$$

EXAMPLE

Aqueous lithium hydroxide solution is used to purify air in spacecrafts and submarines because it absorbs carbon dioxide, which is an end product of metabolism, according to the equation



The pressure of carbon dioxide inside the cabin of a submarine having a volume of 2.4×10^5 L is 7.9×10^{-3} atm at 312 K. A solution of lithium hydroxide (LiOH) of negligible volume is introduced into the cabin. Eventually the pressure of CO_2 falls to 1.2×10^{-4} atm. How many grams of lithium carbonate Li_2CO_3 are formed by this process?

The drop in CO_2 pressure is $(7.9 \times 10^{-3} \text{ atm}) - (1.2 \times 10^{-4} \text{ atm}) = 7.8 \times 10^{-3} \text{ atm}$. Therefore, the number of moles of CO_2 reacted is given by

$$n = P \times \left(\frac{V}{RT} \right)$$

$$\begin{aligned} \Delta n &= 7.8 \times 10^{-3} \text{ atm} \times \frac{2.4 \times 10^5 \text{ L}}{(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(312 \text{ K})} \\ &= 73 \text{ mol} \end{aligned}$$

$1 \text{ mol CO}_2 \approx 1 \text{ mol Li}_2\text{CO}_3$ so the amount of Li_2CO_3 formed is also 73 moles.

$$\begin{aligned} \text{mass of Li}_2\text{CO}_3 \text{ formed} &= 73 \text{ mol Li}_2\text{CO}_3 \times \frac{73.89 \text{ g Li}_2\text{CO}_3}{1 \text{ mol Li}_2\text{CO}_3} \\ &= 5.4 \times 10^3 \text{ g Li}_2\text{CO}_3 \end{aligned}$$

Practice Exercise

Assuming no change in temperature and pressure, calculate the volume of O₂ (in liters) required for the complete combustion of 14.9 L of butane (C₄H₁₀)



Practice Exercise

The equation for the metabolic breakdown of glucose (C₆H₁₂O₆) is the same as the equation for the combustion of glucose in air:



Calculate the volume of CO₂ produced at 37°C and 1.00 atm when 5.60 g of glucose is used up in the reaction.

Practice Exercise

A 2.14-L sample of hydrogen chloride (HCl) gas at 2.61 atm and 28°C is completely dissolved in 668 mL of water to form hydrochloric acid solution. Calculate the molarity of the acid solution. Assume no change in volume.

5.6

Dalton's law of partial pressures

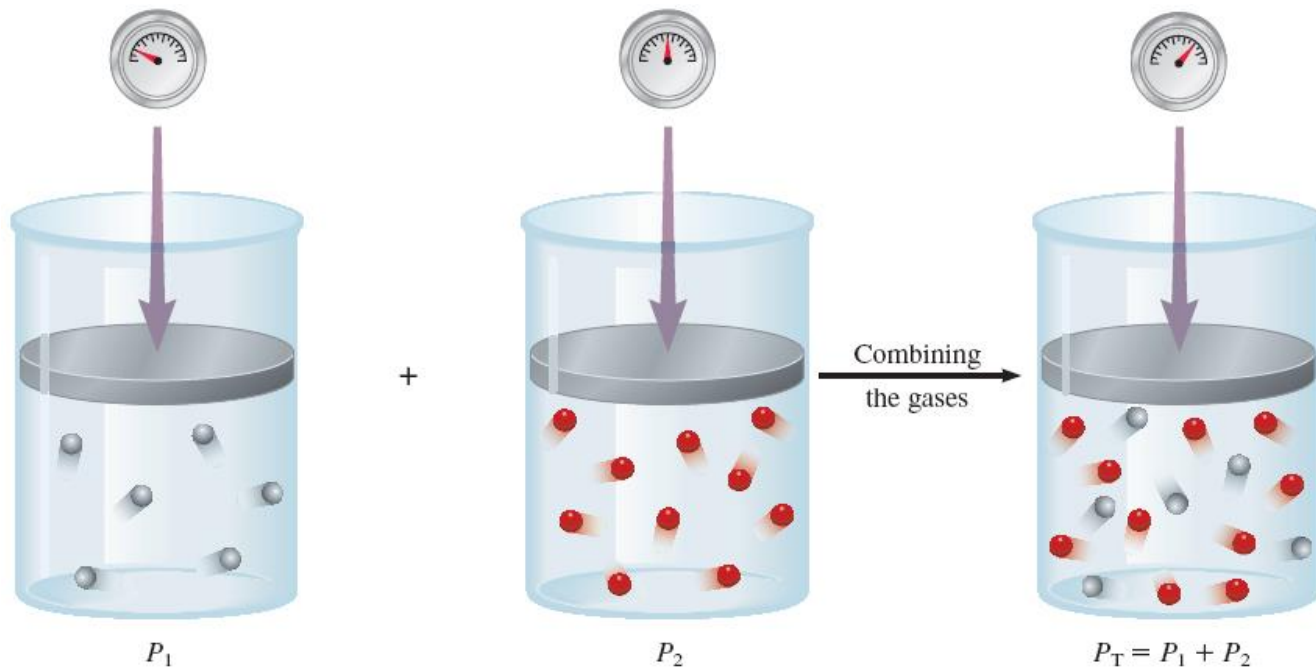
How do we deal with gases composed of a mixture of two or more substances ???

- 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.

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

The pressure exerted by a particular component of a mixture of gases is called the **partial pressure** of that gas.



Consider a case in which two gases, A and B, are in a container of volume V . The pressure exerted by gases A and B, according to the ideal gas equation, is:

$$P_A = \frac{n_A RT}{V} \quad P_B = \frac{n_B RT}{V}$$

In a mixture of gases A and B, the total pressure P_T is the result of the collisions of both types of molecules, A and B, with the walls of the container. Thus, according to Dalton's law,

$$\begin{aligned} P_T &= P_A + P_B \\ &= \frac{n_A RT}{V} + \frac{n_B RT}{V} \\ &= \frac{RT}{V} (n_A + n_B) \\ &= \frac{nRT}{V} \end{aligned}$$

where n , the total number of moles of gases present, is given by $n = n_A + n_B$, and P_A and P_B are the partial pressures of gases A and B, respectively.

For a mixture of gases, then, P_T depends only on the total number of moles of gas present, not on the nature of the gas molecules.

In general, the total pressure of a mixture of gases is given by

$$P_T = P_1 + P_2 + P_3 + \dots$$

where P_1, P_2, P_3, \dots are the partial pressures of components 1, 2, 3,

To see how each partial pressure is related to the total pressure, consider again the case of a mixture of two gases A and B. Dividing P_A by P_T , we obtain

$$\begin{aligned}\frac{P_A}{P_T} &= \frac{n_A RT/V}{(n_A + n_B)RT/V} && \text{where } X_A \text{ is called the mole fraction of A.} \\ &= \frac{n_A}{n_A + n_B} \\ &= X_A\end{aligned}$$

The **mole fraction** is a dimensionless quantity that expresses the ratio of the number of moles of one component to the number of moles of all components present.

$$X_i = \frac{n_i}{n_T}$$

where n_i and n_T are the number of moles of component i and the total number of moles present, respectively.

The mole fraction is always smaller than 1. We can now express the partial pressure as:

$$P_A = X_A P_T \quad P_B = X_B P_T$$

The sum of the mole fractions for a mixture of gases must be unity (1). If only two components are present, then

$$X_A + X_B = \frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = 1$$

If a system contains more than two gases, then the partial pressure of the i th component is related to the total pressure by:

$$P_i = X_i P_T$$

EXAMPLE

A mixture of gases contains 4.46 moles of neon (Ne), 0.74 mole of argon (Ar), and 2.15 moles of xenon (Xe). Calculate the partial pressures of the gases if the total pressure is 2.00 atm at a certain temperature.

$$X_{\text{Ne}} = \frac{n_{\text{Ne}}}{n_{\text{Ne}} + n_{\text{Ar}} + n_{\text{Xe}}} = \frac{4.46 \text{ mol}}{4.46 \text{ mol} + 0.74 \text{ mol} + 2.15 \text{ mol}} = 0.607$$

$$\begin{aligned} P_{\text{Ne}} &= X_{\text{Ne}} P_{\text{T}} \\ &= 0.607 \times 2.00 \text{ atm} \\ &= 1.21 \text{ atm} \end{aligned}$$

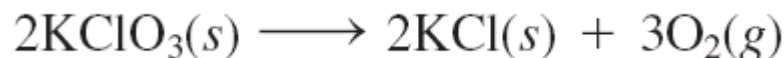
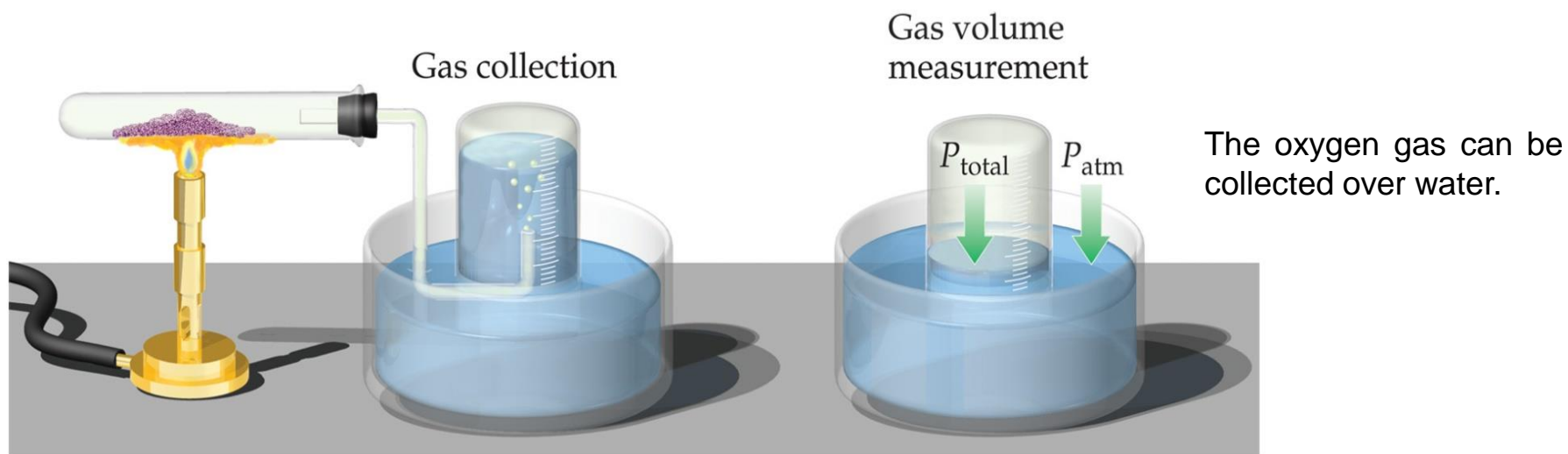
$$\begin{aligned} P_{\text{Ar}} &= X_{\text{Ar}} P_{\text{T}} \\ &= 0.10 \times 2.00 \text{ atm} \\ &= 0.20 \text{ atm} \end{aligned}$$

$$\begin{aligned} P_{\text{Xe}} &= X_{\text{Xe}} P_{\text{T}} \\ &= 0.293 \times 2.00 \text{ atm} \\ &= 0.586 \text{ atm} \end{aligned}$$

$$(1.21 + 0.20 + 0.586) \text{ atm} = 2.00 \text{ atm.}$$

Collecting Gases Over Water

An experiment that is often encountered in general chemistry laboratories involves determining the number of moles of gas collected from a chemical reaction. Sometimes this gas is collected over water.



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.

$$P_{\text{total}} = P_{\text{gas}} + P_{\text{H}_2\text{O}}$$

EXAMPLE

Oxygen gas generated by the decomposition of potassium chlorate is collected over water. The volume of oxygen collected at 24°C and atmospheric pressure of 762 mmHg is 128 mL. Calculate the mass (in grams) of oxygen gas obtained. The pressure of the water vapor at 24°C is 22.4 mmHg.

$$P_T = P_{O_2} + P_{H_2O}$$

$$\begin{aligned} P_{O_2} &= P_T - P_{H_2O} \\ &= 762 \text{ mmHg} - 22.4 \text{ mmHg} \\ &= 740 \text{ mmHg} \end{aligned}$$

From the ideal gas equation

$$PV = nRT = \frac{m}{\mathcal{M}}RT$$

$$\begin{aligned} m &= \frac{PV\mathcal{M}}{RT} = \frac{(740/760)\text{atm}(0.128 \text{ L})(32.00 \text{ g/mol})}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(273 + 24) \text{ K}} \\ &= 0.164 \text{ g} \end{aligned}$$

Practice Exercise

A sample of natural gas contains 8.24 moles of methane (CH_4), 0.421 mole of ethane (C_2H_6), and 0.116 mole of propane (C_3H_8). If the total pressure of the gases is 1.37 atm, what are the partial pressures of the gases?

Practice Exercise

Hydrogen gas generated when calcium metal reacts with water is collected over water. The volume of gas collected at 30°C and pressure of 988 mmHg is 641 mL. What is the mass (in grams) of the hydrogen gas obtained? The pressure of water vapor at 30°C is 31.82 mmHg.

5.7

The kinetic molecular theory of gases

The Kinetic Molecular Theory of Gases

The kinetic molecular theory of gases assumptions:

1. A gas is composed of molecules that are separated from each other by distances far greater than their own dimensions. The molecules can be considered to be “points”; that is, they possess mass but have negligible volume.
2. Gas molecules are in constant motion in random directions, and they frequently collide with one another. Collisions among molecules are perfectly elastic. In other words, energy can be transferred from one molecule to another as a result of a collision. Nevertheless, the total energy of all the molecules in a system remains the same.
3. Gas molecules exert neither attractive nor repulsive forces on one another.
4. The average kinetic energy of the molecules is proportional to the temperature of the gas in kelvins. Any two gases at the same temperature will have the same average kinetic energy. The average kinetic energy of a molecule is given by:

$$\overline{\text{KE}} = \frac{1}{2} m \overline{u^2}$$

where: m is the mass of the molecule and u is its speed.
The horizontal bar denotes an average value.

According to the kinetic molecular theory, gas pressure is the result of collisions between molecules and the walls of their container. It depends on the frequency of collision per unit area and on how “hard” the molecules strike the wall.

Application to the Gas Laws

Compressibility of Gases ...

Because molecules in the gas phase are separated by large distances, gases can be compressed easily to occupy less volume.

Boyle's Law ...

$P \propto$ collision rate with wall

Collision rate \propto number density

Number density $\propto 1/V$

$P \propto 1/V$

Charles's Law ...

$P \propto$ collision rate with wall

Collision rate \propto average kinetic energy of gas molecules

Average kinetic energy $\propto T$

$P \propto T$

Avogadro's Law ...

$P \propto$ collision rate with wall

Collision rate \propto number density

Number density $\propto n$

$$P \propto n$$

Dalton's Law of Partial Pressures ...

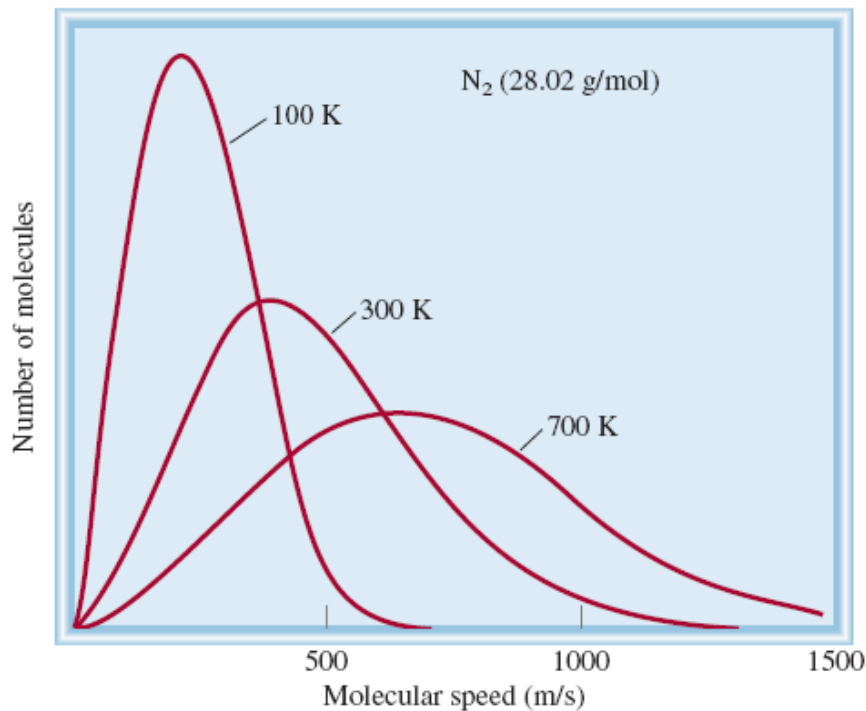
Molecules do not attract or repel one another

P exerted by one type of molecule is unaffected by the presence of another gas

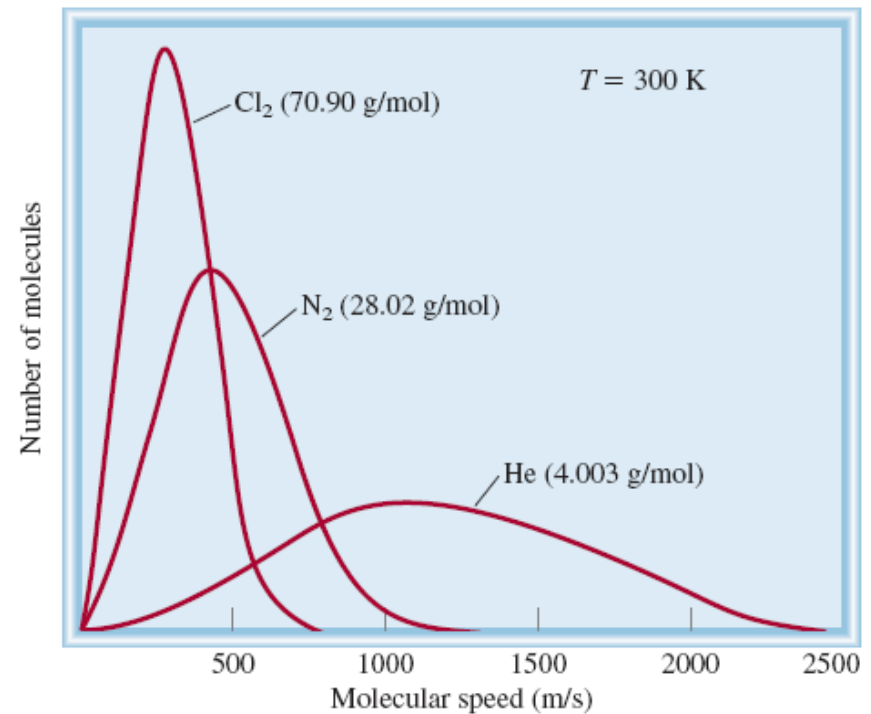
$$P_{\text{total}} = \sum P_i$$

Distribution of Molecular Speeds

The distribution curve tells us the number of molecules moving at a certain speed. The peak of each curve represents the *most probable speed*, that is, the speed of the largest number of molecules.



The distribution of speeds for nitrogen gas at three different temperatures. At the higher temperatures, more molecules are moving at faster speeds.



The distribution of speeds for three gases at 300 K. At a given temperature, the lighter molecules are moving faster, on the average.

Root-Mean-Square Speed

Root-mean-square (*rms*) speed (u_{rms}) is an average molecular speed.

One of the results of the kinetic theory of gases is that the total kinetic energy of a mole of any gas = $\frac{3}{2}RT$.

The average kinetic energy of one molecule = $\frac{1}{2} m\overline{u^2}$

$$u_{rms} = \sqrt{\frac{3RT}{M}}$$

u_{rms} : root-mean-square speed (m/s)

$R = 8.314$ J/K.mol

M : molar mass (kg/mol)

The heavier the gas, the more slowly its molecules move.

EXAMPLE

Calculate the root-mean-square speeds of helium atoms and nitrogen molecules in m/s at 25°C.

Solution:

For **He**: The molar mass of He is 4.003 g/mol, or 4.003×10^{-3} kg/mol.

$$\begin{aligned}u_{\text{rms}} &= \sqrt{\frac{3RT}{M}} \\&= \sqrt{\frac{3(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K})}{4.003 \times 10^{-3} \text{ kg/mol}}} \\&= \sqrt{1.86 \times 10^6 \text{ J/kg}}\end{aligned}$$

Using the conversion factor:

$$1 \text{ J} = 1 \text{ kg m}^2/\text{s}^2$$

$$\begin{aligned}u_{\text{rms}} &= \sqrt{1.86 \times 10^6 \text{ kg m}^2/\text{kg} \cdot \text{s}^2} \\&= \sqrt{1.86 \times 10^6 \text{ m}^2/\text{s}^2} \\&= 1.36 \times 10^3 \text{ m/s}\end{aligned}$$

For **N₂**: the molar mass is 28.02 g/mol, or 2.802×10^{-2} kg/mol

$$\begin{aligned}u_{\text{rms}} &= \sqrt{\frac{3(8.314 \text{ J/K} \cdot \text{mole})(298 \text{ K})}{2.802 \times 10^{-2} \text{ kg/mol}}} \\&= \sqrt{2.65 \times 10^5 \text{ m}^2/\text{s}^2} \\&= 515 \text{ m/s}\end{aligned}$$

Practice Exercise

Calculate the root-mean-square speed of molecular chlorine in m/s at 20°C.

Gas Diffusion and Effusion

Gas Diffusion

The gradual mixing of molecules of one gas with molecules of another by virtue of their kinetic properties.

Thomas Graham found that under the same conditions of temperature and pressure, rates of diffusion for gases are inversely proportional to the square roots of their molar masses.



The path traveled by a single gas molecule.
Each change in direction represents a collision with another molecule.

Graham's law of diffusion

$$\frac{r_1}{r_2} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}}$$

where r_1 and r_2 are the diffusion rates of gases 1 and 2, and \mathcal{M}_1 and \mathcal{M}_2 are their molar masses, respectively.



A demonstration of gas diffusion. NH_3 gas (from a bottle containing aqueous ammonia) combines with HCl gas (from a bottle containing hydrochloric acid) to form solid NH_4Cl . Because NH_3 is lighter and therefore diffuses faster, solid NH_4Cl first appears nearer the HCl bottle (on the right).

HCl : 36 g/mol

NH_3 : 17 g/mol

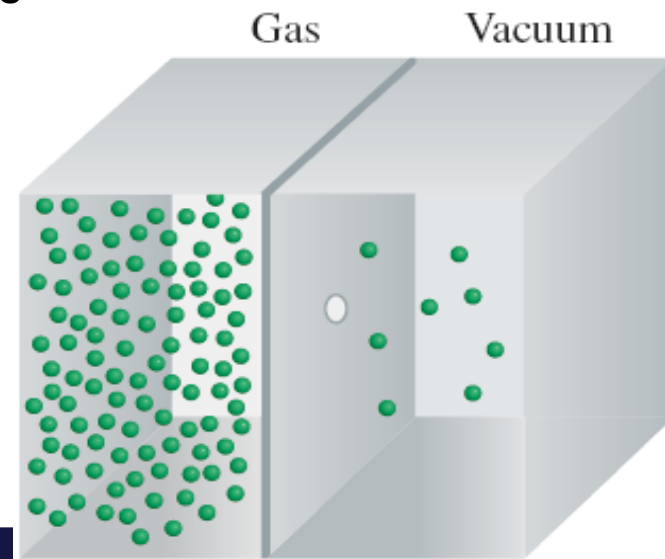
Gas Effusion

The process by which a gas under pressure escapes from one compartment of a container to another by passing through a small opening.

Although effusion differs from diffusion in nature, the rate of effusion of a gas has the same form as Graham's law of diffusion.

$$\frac{r_1}{r_2} = \frac{t_2}{t_1} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}}$$

where t_1 and t_2 are the times for effusion for gases 1 and 2, respectively.



EXAMPLE

A flammable gas made up only of carbon and hydrogen is found to effuse through a porous barrier in 1.50 min. Under the same conditions of temperature and pressure, it takes an equal volume of bromine vapor 4.73 min to effuse through the same barrier. Calculate the molar mass of the unknown gas, and suggest what this gas might be.

Solution:

From the molar mass of Br₂

$$\frac{1.50 \text{ min}}{4.73 \text{ min}} = \sqrt{\frac{\mathcal{M}}{159.8 \text{ g/mol}}}$$

$$\begin{aligned}\mathcal{M} &= \left(\frac{1.50 \text{ min}}{4.73 \text{ min}}\right)^2 \times 159.8 \text{ g/mol} \\ &= 16.1 \text{ g/mol}\end{aligned}$$

Because the molar mass of carbon is 12.01 g and that of hydrogen is 1.008 g, the gas is methane (CH₄).

EXAMPLE

Nickel forms a gaseous compound of the formula $\text{Ni}(\text{CO})_x$. What is the value of x given that under the same conditions methane (CH_4) effuses 3.3 times faster than the compound?

Solution

The molar mass of CH_4 is 16 g and that of Ni is 58.7 g

$$\frac{r_1}{r_2} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}} \quad r_1 = 3.3 \times r_2 \quad \mathcal{M}_2 = \left(\frac{r_1}{r_2}\right)^2 \times \mathcal{M}_1$$

$$= (3.3)^2 \times 16 = 174.2$$

$$58.7 + (x \cdot 28) = 174.2$$

$$x = 4.1 \sim 4$$

Practice Exercise

It takes 192 s for an unknown gas to effuse through a porous wall and 84 s for the same volume of N_2 gas to effuse at the same temperature and pressure. What is the molar mass of the unknown gas?

5.8

Deviation from ideal behavior

Deviations from Ideal Behavior

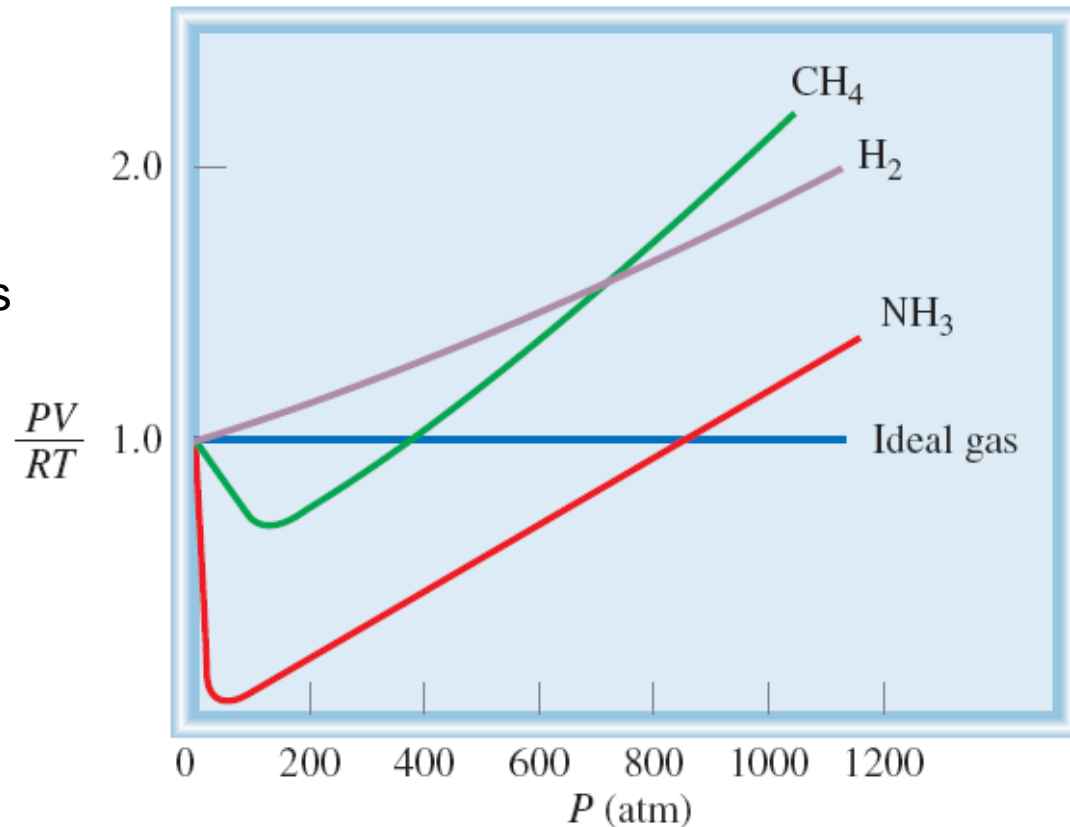
Although we can assume that real gases behave like an ideal gas, we cannot expect them to do so under all conditions.

According to the ideal gas equation,
for 1 mole of gas,

$$PV / RT = 1$$

regardless of the actual gas pressure and temperature.

Significant deviations occur as pressure increases or temperature decrease.

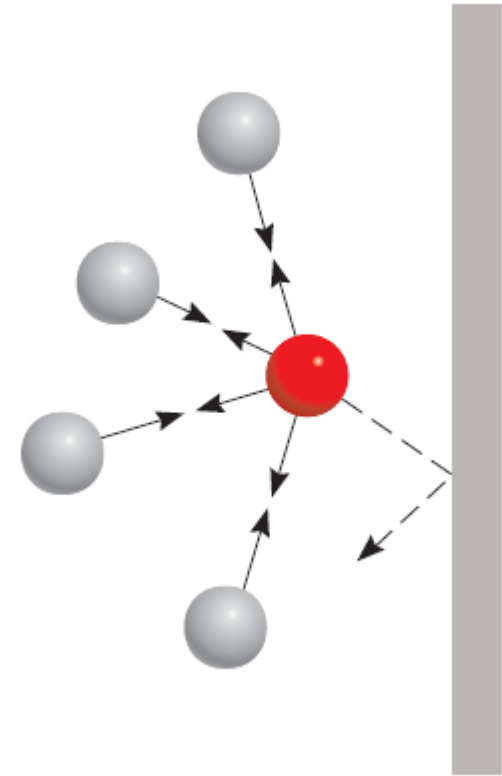


Van der Waals equation

nonideal gas

Having taken into account the corrections for pressure and volume, we can rewrite the ideal gas equation as follows:

$$\underbrace{\left(P + \frac{an^2}{V^2} \right)}_{\text{corrected pressure}} \underbrace{(V - nb)}_{\text{corrected volume}} = nRT$$



Effect of intermolecular forces on the pressure exerted by a gas.

van der Waals constants of some common gases

The value of a indicates how strongly molecules of a given type of gas attract one another. Helium atoms have the weakest attraction for one another, because helium has the smallest a value.

There is also a rough correlation between molecular size and b . Generally, the larger the molecule (or atom), the greater b is, but the relationship between b and molecular (or atomic) size is not a simple one.

| Gas | a $\left(\frac{\text{atm} \cdot \text{L}^2}{\text{mol}^2}\right)$ | b $\left(\frac{\text{L}}{\text{mol}}\right)$ |
|------------------|--|---|
| He | 0.034 | 0.0237 |
| Ne | 0.211 | 0.0171 |
| Ar | 1.34 | 0.0322 |
| Kr | 2.32 | 0.0398 |
| Xe | 4.19 | 0.0266 |
| H ₂ | 0.244 | 0.0266 |
| N ₂ | 1.39 | 0.0391 |
| O ₂ | 1.36 | 0.0318 |
| Cl ₂ | 6.49 | 0.0562 |
| CO ₂ | 3.59 | 0.0427 |
| CH ₄ | 2.25 | 0.0428 |
| CCl ₄ | 20.4 | 0.138 |
| NH ₃ | 4.17 | 0.0371 |
| H ₂ O | 5.46 | 0.0305 |

EXAMPLE

Given that 3.50 moles of NH_3 occupy 5.20 L at 47°C , calculate the pressure of the gas (in atm) using (a) the ideal gas equation and (b) the van der Waals equation.

Solution:

$$V = 5.20 \text{ L}, \quad T = (47 + 273) \text{ K} = 320 \text{ K}, \quad n = 3.50 \text{ mol}, \quad R = 0.0821 \text{ L}\cdot\text{atm}/\text{K}\cdot\text{mol}$$

(a) Using the ideal gas equation,

$$\begin{aligned} P &= \frac{nRT}{V} \\ &= \frac{(3.50 \text{ mol})(0.0821 \text{ L}\cdot\text{atm}/\text{K}\cdot\text{mol})(320 \text{ K})}{5.20 \text{ L}} \\ &= 17.7 \text{ atm} \end{aligned}$$

(b) Using the van der Waals equation,

$$\begin{aligned} \frac{an^2}{V^2} &= \frac{(4.17 \text{ atm}\cdot\text{L}^2/\text{mol}^2)(3.50 \text{ mol})^2}{(5.20 \text{ L})^2} = 1.89 \text{ atm} \\ nb &= (3.50 \text{ mol})(0.0371 \text{ L/mol}) = 0.130 \text{ L} \end{aligned}$$

For NH_3 ;

$$a = 4.17 \text{ atm}\cdot\text{L}^2/\text{mol}^2, \quad b = 0.0371 \text{ L/mol}$$

$$\begin{aligned} (P + 1.89 \text{ atm})(5.20 \text{ L} - 0.130 \text{ L}) &= (3.50 \text{ mol})(0.0821 \text{ L}\cdot\text{atm}/\text{K}\cdot\text{mol})(320 \text{ K}) \\ P &= 16.2 \text{ atm} \end{aligned}$$

Practice Exercise

Using the data shown in the van der Waals constants Table, calculate the pressure exerted by 4.37 moles of molecular chlorine confined in a volume of 2.45 L at 38°C . Compare the pressure with that calculated using the ideal gas equation.

