Chemistry, The Central Science, 10th edition
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and Bruce E. Bursten

Chapter 10
Gases

The things we will cover in this chapter:

- How Gases differ from solids and liquids
- Pressure, its units and earths atmosphere
- Volume temperature pressure and amount of gas
- Ideal gases
- Kinetic molecular theories of gas
- Effusion and diffusion
- Real gases and ideal gases- van der Waals equation

The Air Around Us

- 78% N_2
- 21% O_2 and
- A small amount of other gases.

Characteristics of Gases

- Unlike liquids and solids, they
  - Expand to fill their containers.
  - Are highly compressible.
  - Have extremely low densities.

- Substances that are solids or liquids under ordinary conditions can exist as gases too.
- In that state they are referred as vapors.

Example: Water vapor, Mercury vapor

- Gases form homogeneous mixtures regardless of their identities.
- Non miscible liquids in their vapor form are totally homogenous mixtures.
- For example water and gasoline that are not miscible in each other, mix completely in their vapor form.

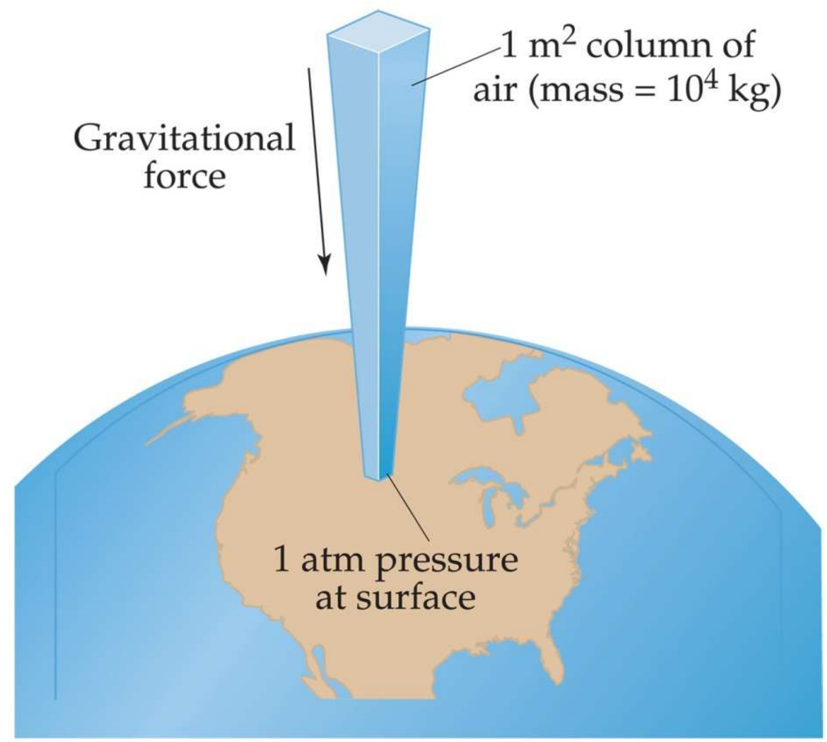
- This is because of the fact that the gas molecules are so far apart they do not influence each other.

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.



To calculate the atmospheric pressure:

- Force = Mass x Acceleration

  Acceleration here is the gravitational force

  $= 9.8 m/s^2$

A column of atmosphere of I m^2 area is about 10,000kg

So the **force** exerted by the column is

$=10,000$ Kg x $9.8\ m/s^2$

$= 1 \times 10^5$ $Kg.m/s^2$

$= 1 \times 10^5$ N or Newton (the SI unit for pressure)

Therefore

Pressure which is F/A $= 1 \times 10^5$ Newton/ 1 m^2

$= 1 \times 10^5$ Pa (=1 bar)

$=1 \times 10^2$ kPa

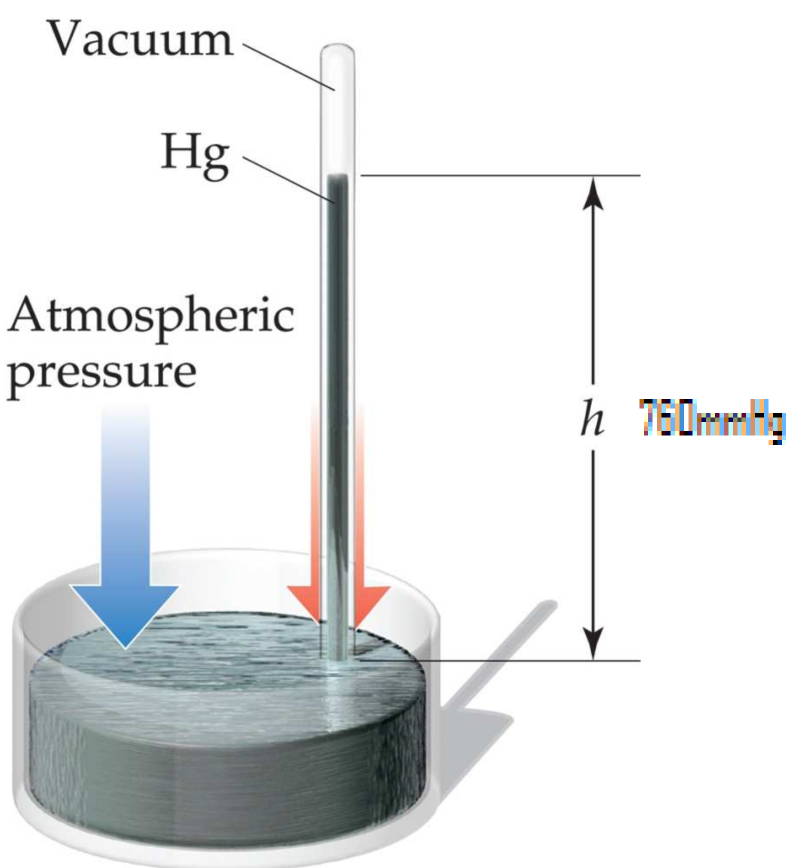
Atmospheric Pressure

The experiment to prove that the atmosphere has weight was first conducted by Torricelli.

Pascal was one of the first to confirm the finding.

1.00 atm = 760 mm of mercury

- mm Hg or torr are the same thing



Units of Pressure

- Pascals (SI unit for pressure)

  1 Pa = 1 N/m^2

- Bar

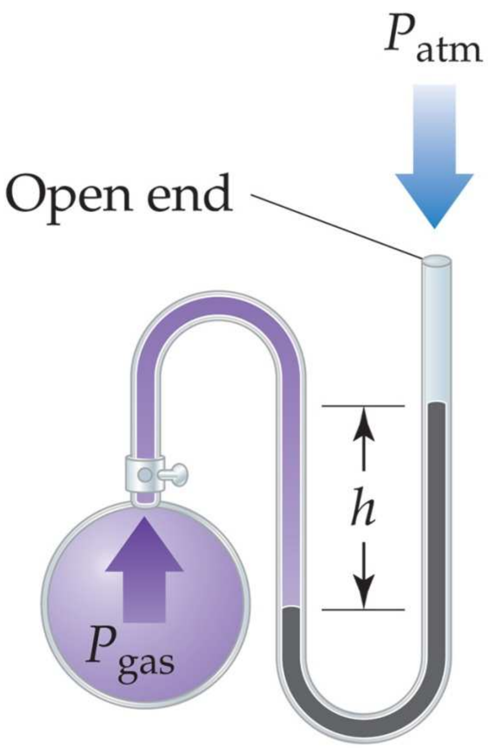
  1 bar = 10^5 Pa = 100 kPa

1 atm = 760 mm Hg = 760 torr = 1.01325x 10^5 Pa = 101.325 kPa
= 1 Bar

You need to memorize this

Find the relationship between atm and N/m^2

Manometer

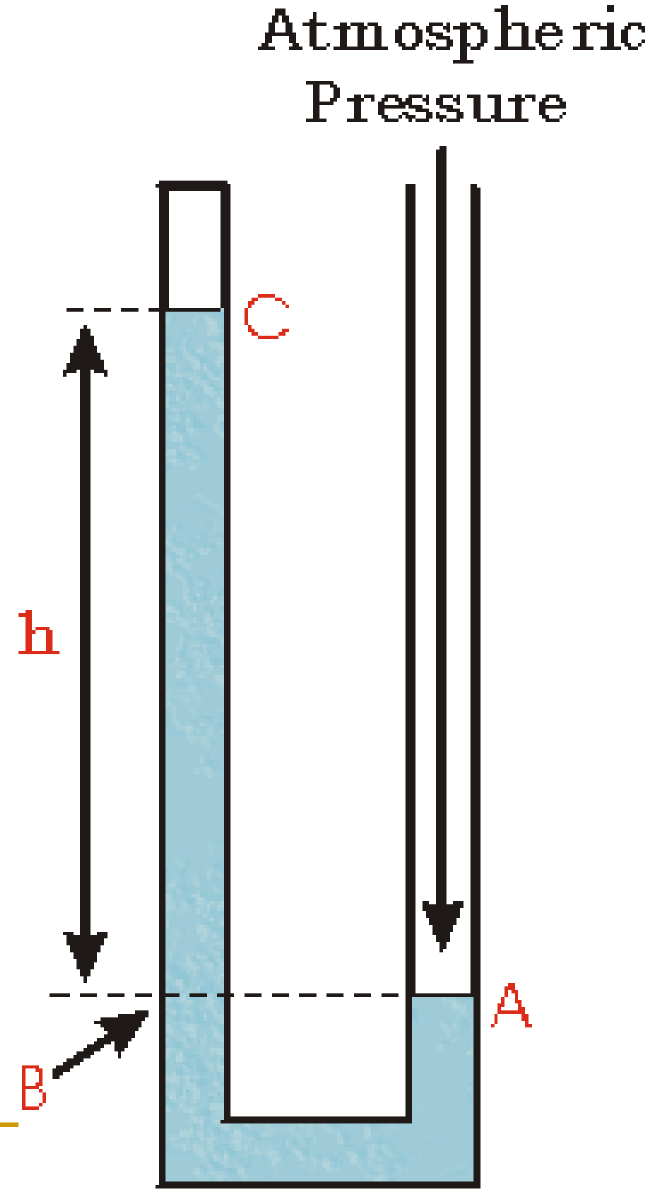


$$P_{gas} = P_{atm} + P_h$$

Used to measure the difference in pressure between atmospheric pressure and that of a gas in a vessel.

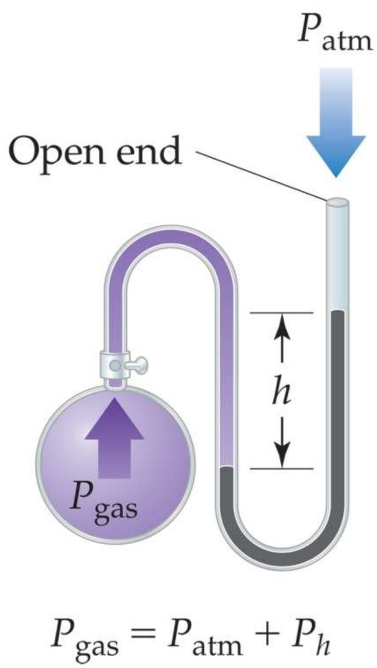
Closed ended manometer:

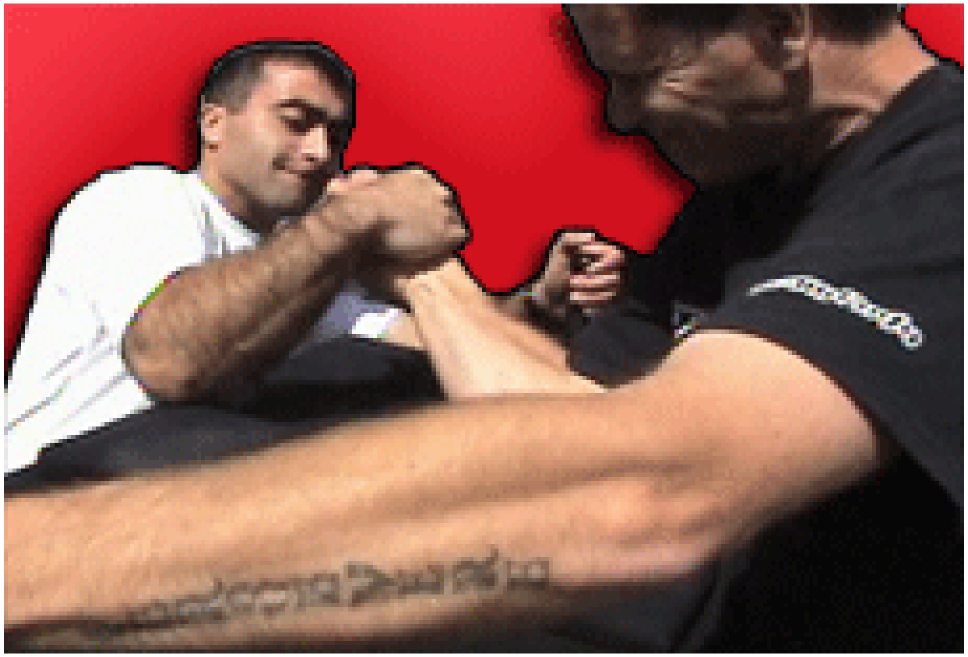
- The point A is at atmospheric pressure.
- The point C is at whatever pressure the gas in the closed end of the tube has, or if the closed end contains a vacuum the pressure is zero.
- Since the point B is at the same height as point A, it must be at atmospheric pressure too. But the pressure at B is also the sum of the pressure at C plus the pressure exerted by the weight of the column of liquid of height h in the tube.



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?





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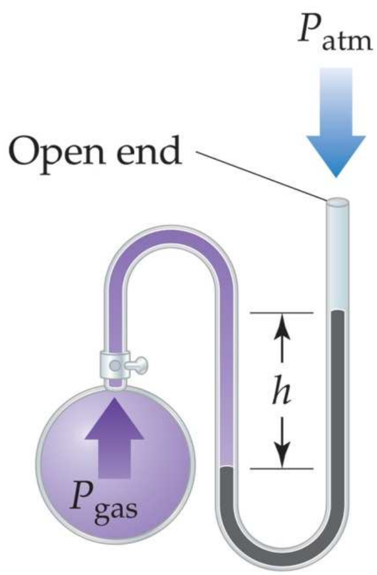

$$P_{gas} = P_{atm} + P_h$$

- 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

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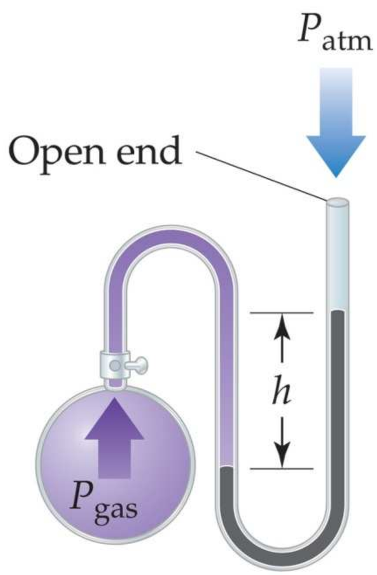


$P_{gas} = P_{atm} + P_h$

Solve: (a) The pressure of the gas :

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

We convert the pressure of the gas to atmospheres:

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

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

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

Standard Pressure

- Normal atmospheric pressure at sea level.
  - It is equal to
    - 1.00 atm
    - 760 torr (760 mm Hg)
    - 101.325 kPa

- Problem number 10.23

Homework problem

I will collect this on Monday, in the first ten minutes of the class.

I will not accept late submissions under any circumstances.

Come to the class on time!

This will be your attendance for the day.

How high in meters should a column of water be to exert the pressure equal to that of a 760 mm column of mercury.

Pressure = Force/ area

F = mass x acceleration

$$\text{Pressure} = \frac{\text{mass x acceleration}}{\text{area}}$$

$$\frac{\text{Mass (Hg) x g}}{\text{area}} = \frac{\text{mass (water) x g}}{\text{area}}$$

Mass (hg) = Mass (water)

D=m/V m=DV V= l x w x h = area x h

D(Hg) x h(Hg) = D (water) x h (water)

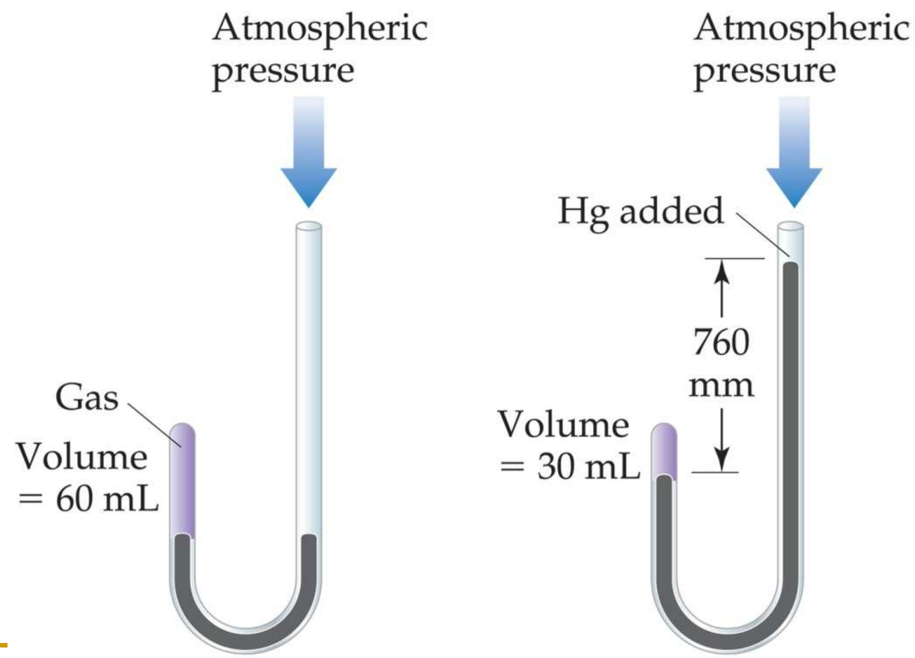
$$\text{h(water)} = \frac{\text{D(Hg) x h(Hg)}}{\text{D(water)}} =$$

- 1) In a Torricelli barometer, a pressure of one atmosphere supports a 760 mm column of mercury. If the original tube containing the mercury is replaced with a tube having twice the diameter of the original, the height of the mercury column at one atmosphere pressure is __________ mm.

Boyle's Law

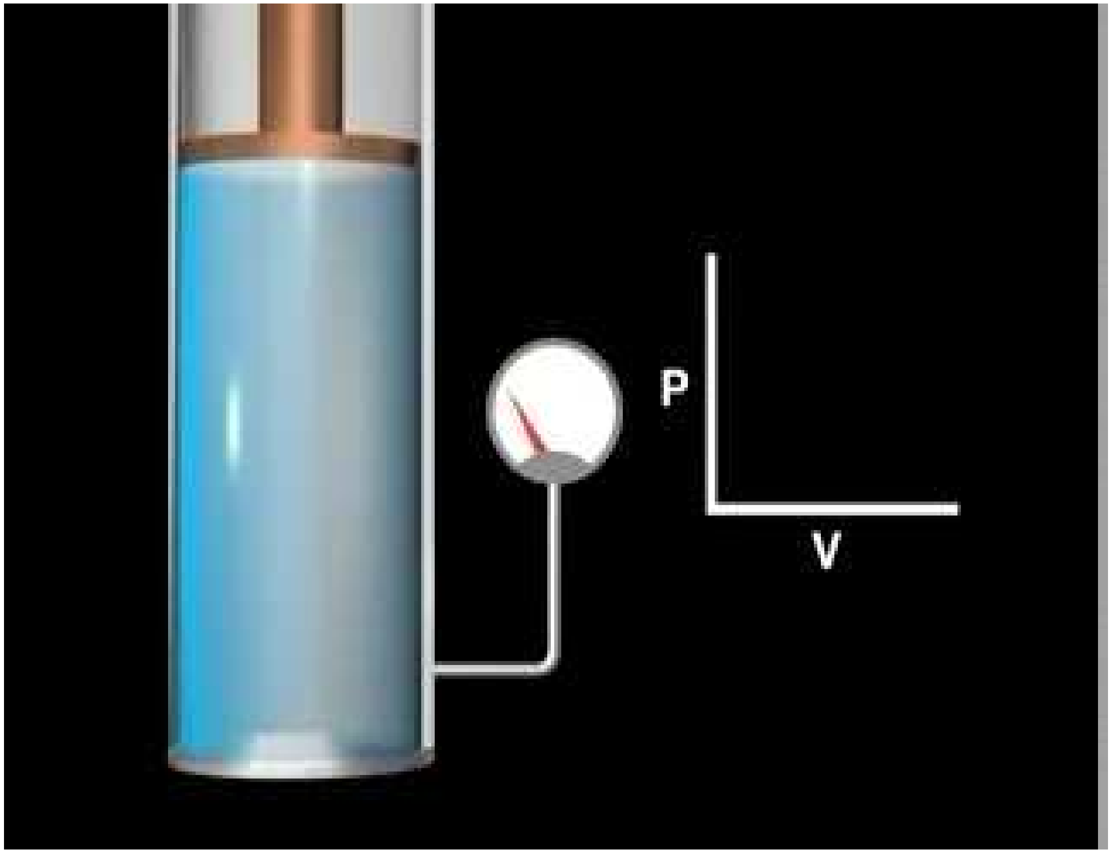
Robert Boyle (1627-1691)

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



- Boyle holds a special place in science as his experiment was the first one where a very systematic study was done in which one variable was changed to see the effect on another variable.

Boyle's Law



$$V \propto \frac{1}{P} \qquad V = \text{Constant} \times \frac{1}{P}$$

$$PV = \text{constant}$$

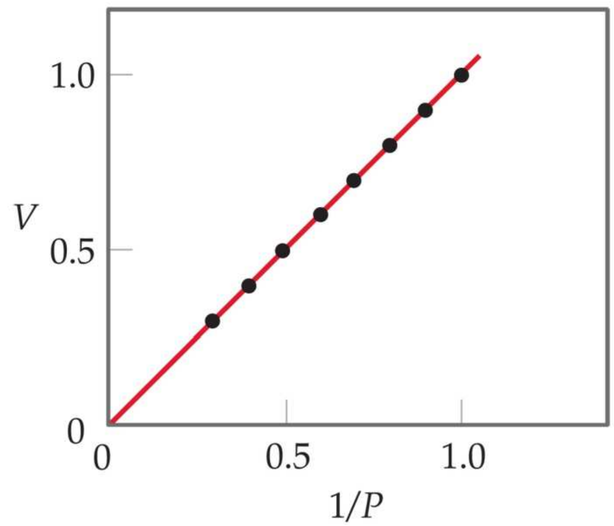
- The value of the constant depends on the temperature and the amount of gas in the sample.

As *P* and *V* are inversely proportional

Since $PV = k$

- *And* $V = k\,(1/P)$

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



Charles's Law (1787)

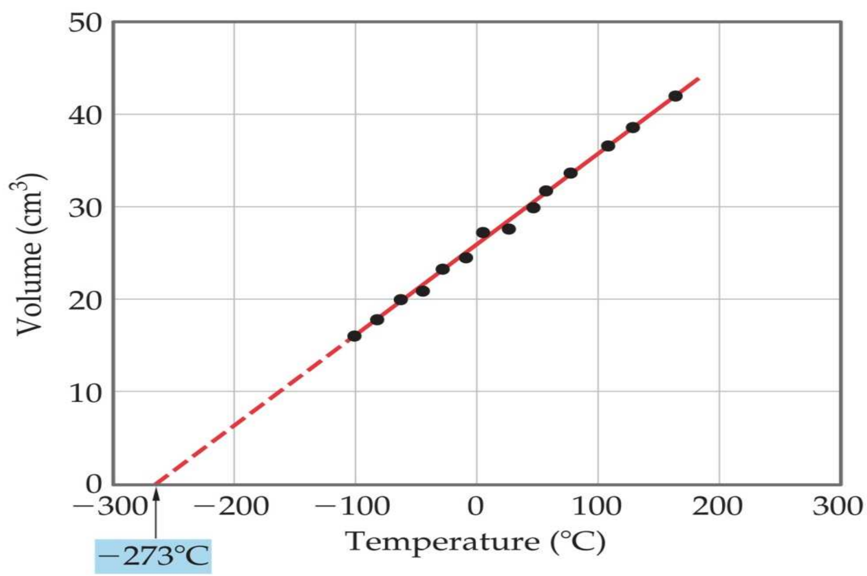
Jacques Charles 1746-1823

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

$V \propto T$

$V = kT$

the value of k depends on pressure and the amount of gas



- i.e., $\frac{V}{T} = k$

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

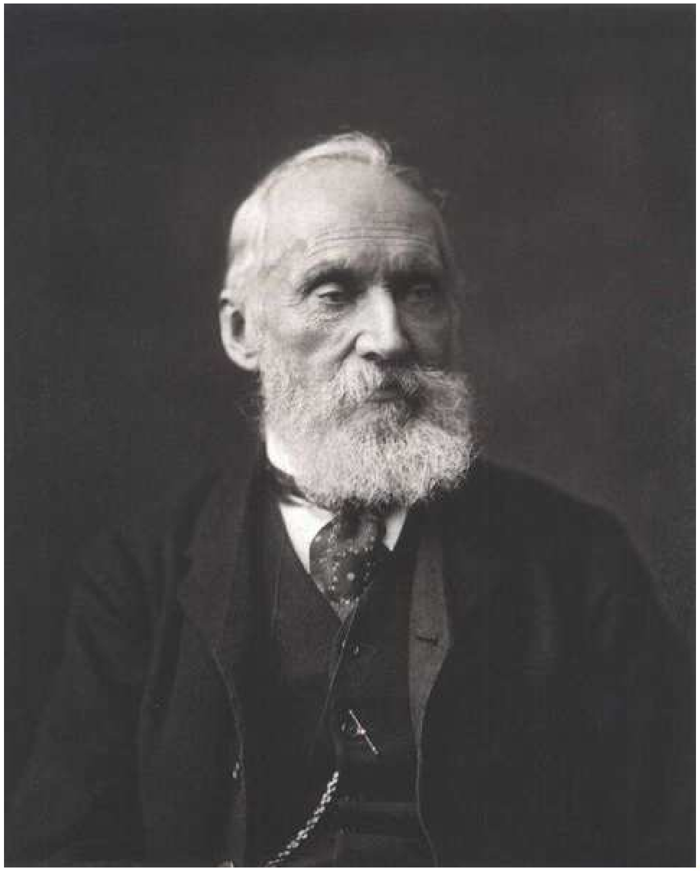
Something about Lord Kelvin (actual name William Thomson)

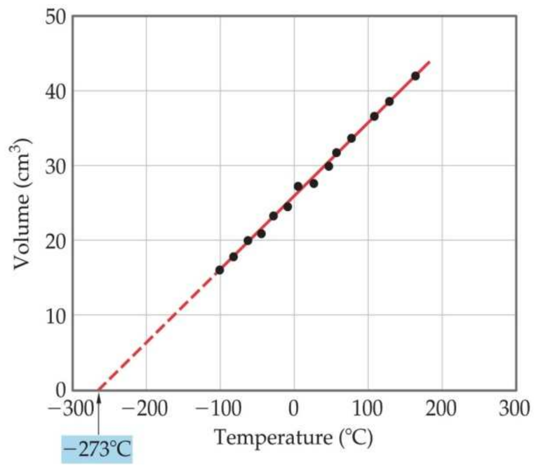
1824- 1907

In 1848 He proposed the Kelvin scale

0 K is -273.15 ^{o}C

It is the temperature at which all atomic motion comes to a complete stop.





- In theory at -273^{o}C all gases should have a volume of zero but the situation is never realized as the gases turn to solids or liquids before reaching this temperature.

- You see the temperature volume relationship in your car tires.

- The temperature in gas equations is always in Kelvin.
- If it is given to you in Celsius, you must convert it into Kelvin by adding ……………..

Avogadro's Hypothesis

- Equal volumes of gases at the same temperature and pressure contain equal number of molecules.
- At $0^{o}C$ and 1 atm pressure (STP) 22.4 L of any gas has 6.02×10^{23} (one mole) molecules.

Volume	22.4 L	22.4 L	22.4 L
Pressure	1 atm	1 atm	1 atm
Temperature	0°C	0°C	0°C
Mass of gas	4.00 g	28.0 g	16.0 g
Number of gas molecules	6.02×10^{23}	6.02×10^{23}	6.02×10^{23}

Avogadro's Law

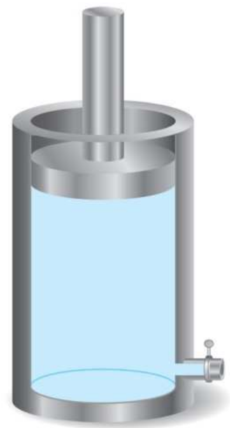
- The volume of a gas at constant temperature and pressure is directly proportional to the number of moles of the gas.

- $V \propto n$
- $V = kn$

SAMPLE EXERCISE 10.3 Evaluating the Effects of Changes in P, V, n, and T on a Gas

Suppose we have a gas confined to a cylinder as shown in Figure 10.12. Consider the following changes:

(a) Heat the gas from 298 K to 360 K, **while maintaining the piston in the position** shown in the drawing.
How will this effect the average distance between the molecules, the pressure of the gas and the number of moles of the gas.



(a) Heating the gas while maintaining the position of the piston will cause no change in the number of molecules per unit volume. Thus, the distance between molecules and the total moles of gas remain the same.

The increase in temperature, however, will cause the pressure to increase (Charles's law).

(b) Move the piston to reduce the volume of gas from 1 L to 0.5 L.

The total number of molecules of gas, and thus the total number of moles, remains the same.

Moving the piston compresses the same quantity of gas into a smaller volume.

The reduction in volume causes the pressure to increase (Boyle's law).

(c) Inject additional gas through the gas inlet valve.

(c) will result in more molecules and thus a greater number of moles of gas.

The average distance between atoms must decrease because their number per unit volume increases.

Correspondingly, the pressure increases.

Ideal-Gas Equation

- So far we've seen that

  $V \propto 1/P$ (Boyle's law)

  $V \propto T$ (Charles's law)

  $V \propto n$ (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

$$PV = nRT$$

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Ideal-Gas Equation

$PV = nRT$

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

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

This can have many units depending on the units of P, V, n and T

TABLE 10.2 Numerical Values of the Gas Constant, *R*, in Various Units

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 work involved in the compression –expansion of gases is called pressure volume work.

  (Chapter 5)

  Therefore the units for PV can be Joules or calories.

- 0^oC and 1 atm are referred to as standard temperature and pressure (STP).

To Calculate the Volume of One Mole of Gas at STP(0^oC and 1 atm).

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

P= 1.000 atm

n = 1.000 mole

T = 0.00^oC = 273.15 K

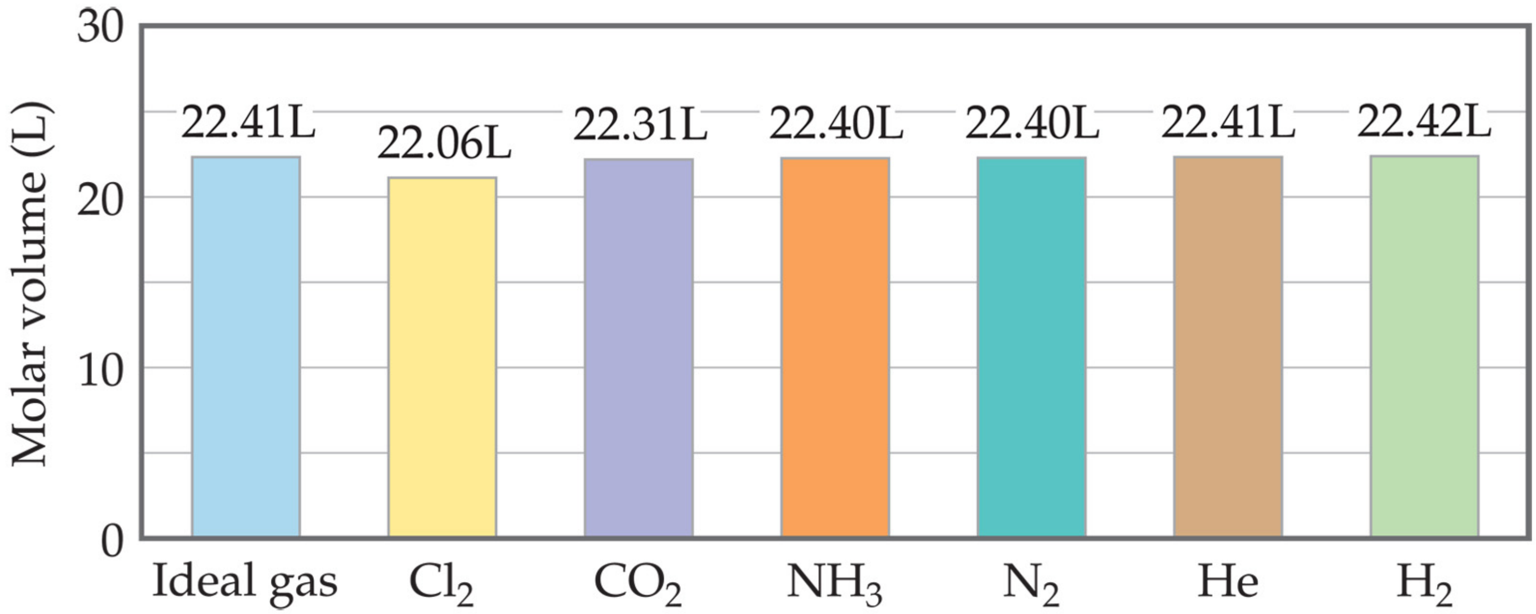
$$V = \frac{(1.000\text{mole}) \times (0.08206 \text{ L atm /mol-K})(273.15\text{K})}{1.000 \text{ atm}}$$

= 22.414689 L

= 22.41 L (with correct number of significant figures)

- You need to remember this value of 22.4 L for one mole of any gas at STP.

- For real gases the volume is close to the calculated value



- 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℃. How m any moles of CO_2 gas were generated?

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

Absolute temperature must always be used when the ideal-gas equation is solved. The other units need to be changed to match the unit of R.

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

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

- Tennis balls are usually filled with air or N_2 gas to a pressure above atmospheric pressure to increase their "bounce." If a particular tennis ball has a volume of 144 cm^3 and contains 0.33 g of N_2 gas, what is the pressure inside the ball at 24℃?

- Volume = 144cm^3 =? L
- Mass = 0.33g = ? Moles
- Temp = 24^oC =? K
- R = 0.0821atm.L/mole K

- PV=nRT
- P = nRT/V

Answer: 2.0 atm

Ideal Gas

- Ideal gas is a hypothetical gas whose pressure, volume and temperature behavior are completely followed by the ideal gas equation.

Relating the Ideal Gas Equation and the Gas Law

- $PV = nRT$
- When the temperature and the quantity of the gas are kept constant

$$PV = \text{Constant}$$

This is Boyle's law.

So

$$P_1V_1 = P_2V_2$$

- When n and V are constant:

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

$$\frac{P_1}{T_1}=\frac{P_2}{T_2}\text{ and so on}$$

$$\frac{PV}{T}=nR=\text{constant}$$

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

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?

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

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

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

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

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

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

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 28,500 ft^3. What is the volume of the same quantity of gas on a warm July day when the temperature is 31°C (88°F)?

Given

Pressure = 2.20 atm which is constant

At Temperature = - 15^oC the Volume = 28,500 Ft^3

Asked

When is Temp= 31^oC, Volume = ?

PV=nRT

V/T=nR/P

$$\frac{V1}{T1} = \frac{V2}{T2}$$

$$\frac{V1T2}{T1} = V2$$

Answer= 33,600 ft3

Densities of Gases

By rearranging the ideal gas equation we get

$$\frac{n}{V} = \frac{P}{RT}$$

So multiplying both sides of the equation by the molar mass (M) gives

$$\frac{Mn}{V} = \frac{PM}{RT}$$

$$Mn = \frac{grams}{moles} x moles$$

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

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

- Density is higher
  1. for gases with a higher molar mass
  2. at higher pressures
  3. at lower temperatures

What is more dense – water vapor or nitrogen gas and why?

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

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

We must convert temperature to the Kelvin scale and pressure to atmospheres.

The molar mass of CCl_4 is 12.0 + (4)(35.5) = 154.0g/mol.

- R=0.0821 L atm / mole K

$$d = \frac{(714\text{ torr})(1\text{ atm}/760\text{ torr})(154.0\text{ g/mol})}{\text{om}(0.0821\text{ L-atm/mol-K})(398\ K)} = 4.43\text{ g/L}$$

Molecular Mass

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

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

Becomes

$$M = \frac{dRT}{P}$$

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.

A series of measurements are made in order 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.) Assuming that the ideal-gas equation applies, calculate the molar mass of the unknown gas.

$$\mathcal{M} = \frac{dRT}{P}$$

Given : Temperature and Pressure
Mass of empty and Full flask (mass of air within)
Mass of a flask full of water
Density of water

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:

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

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:

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

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

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

SAMPLE EXERCISE 10.8 continued

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 Kelvin, we can use Equation 10.11 to calculate the molar mass:

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

Volume of Gases in Chemical Reactions

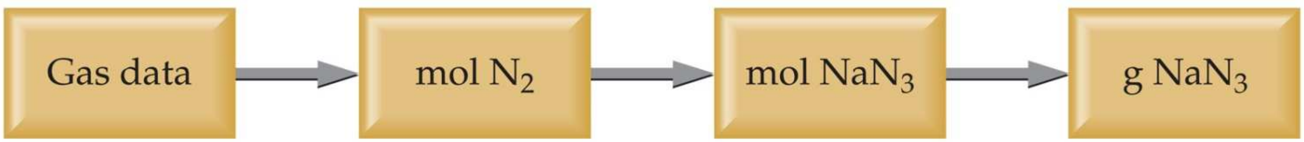
The safety air bags in automobiles are inflated by nitrogen gas generated by the rapid decomposition of sodium azide, NaN_3:

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

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℃, how many grams of NaN_3 must be decomposed?

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.

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

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

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,

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

- Total Pressure Pt =P1+P2+ P3…………

$$PV = nRT$$

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

$P1 = \frac{n1RT}{V}$; $P2 = \frac{n2RT}{V}$ and so on…………

$Pt = (n1+n2+n2……)\frac{RT}{V}$ = nt (RT/V)

The total pressure at constant T and V is determined by the total number of moles of gas present, it is not important if it is just one gas or a mixture of many gases.

Partial Pressure and Mole Fractions

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

As each gas in a mixture behaves independently we can relate the amount of the given gas in a mixture with it partial pressure.

$$\frac{P1}{Pt} = \frac{\frac{n1RT}{V}}{\frac{ntRT}{V}} = \frac{n1}{nt}$$

Pt= total pressure

$$P1 = \frac{n1Pt}{nt}$$

n_1/n_t is called the mole **fraction X**

So $P_1 = X_1 P_t$

- Mole fraction X

$$= \frac{\text{moles of component}}{\text{total moles of all the components}}$$

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.

What is mol fraction = $$\frac{n_1}{n_{total}}$$

What is mol percent = $$\frac{n_1}{n_{total}} x100$$

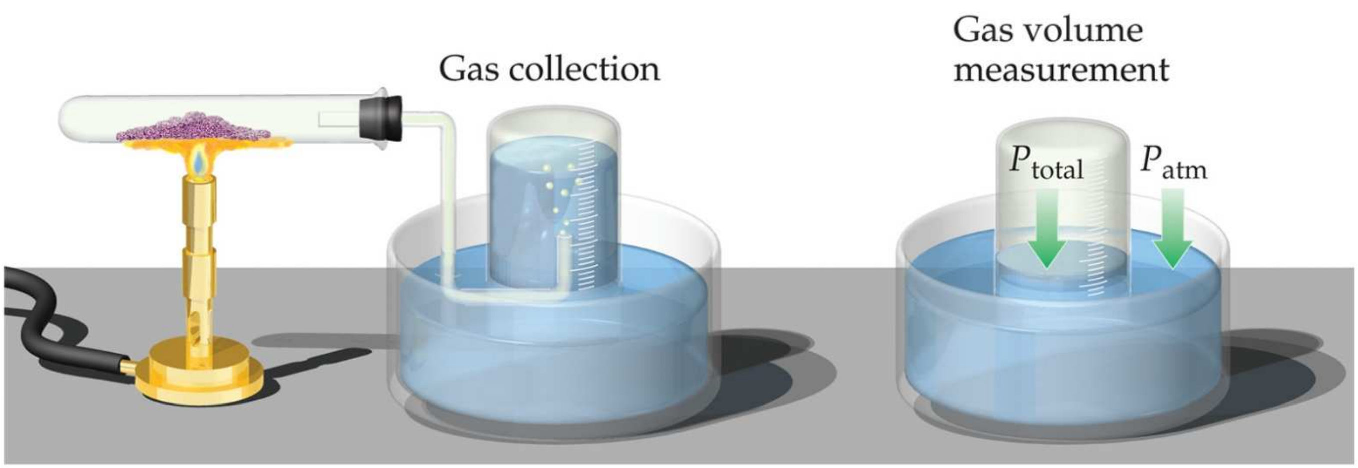
So mole percent /100 is mole fraction.

And then $P_1 = X1\ P_t$

Answer: 1.0×10^3 torr N_2, 1.5×10^2 torr Ar, and 73 torr CH_4

Gases

Partial Pressures



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

$$P_{total} = P_{gas} + P_{H2O}$$

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

$$P_{gas} = P_{total} - P_{H2O}$$

P_{H20} at that temperature will be given to you

A sample of $KClO_3$ is partially decomposed producing O_2 gas that is collected over water. 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?

$$2KClO_3\ (s) \rightarrow 2KCl\ (s) + 3O_2\ (g)$$

a) $P_{gas} = P_{total} - P_{H2O}$ The value of P_{H2O} at the given temperature comes form a table

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

then calculate n with $n = \frac{PV}{RT}$ for O_2

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

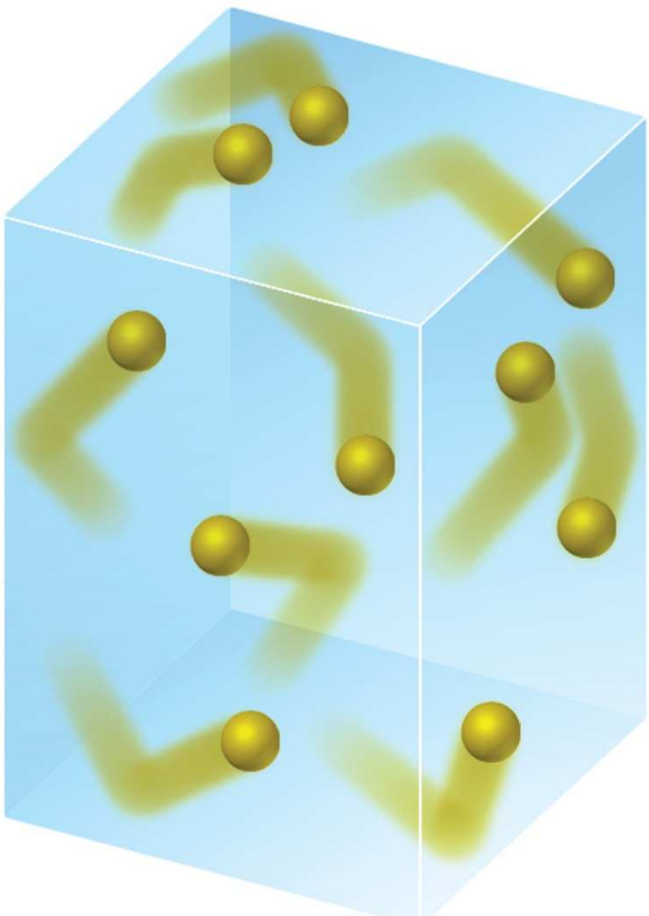
Then for b) do the stoichiometric calculation to get moles of $KClO_3$

Then convert it to g of $KClO_3$

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

- In the last semester 60% of the students forgot to subtract the vapor pressure of water from the total pressure.
- Please remember this during your exam.

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

Gases consist of large numbers of molecules (or atoms) that are in continuous, random motion.

Main Tenets of Kinetic-Molecular Theory

- The combined volume of all the molecules of the gas is negligible relative to the total volume in which the gas is contained.
- Attractive and repulsive forces between gas molecules are negligible.

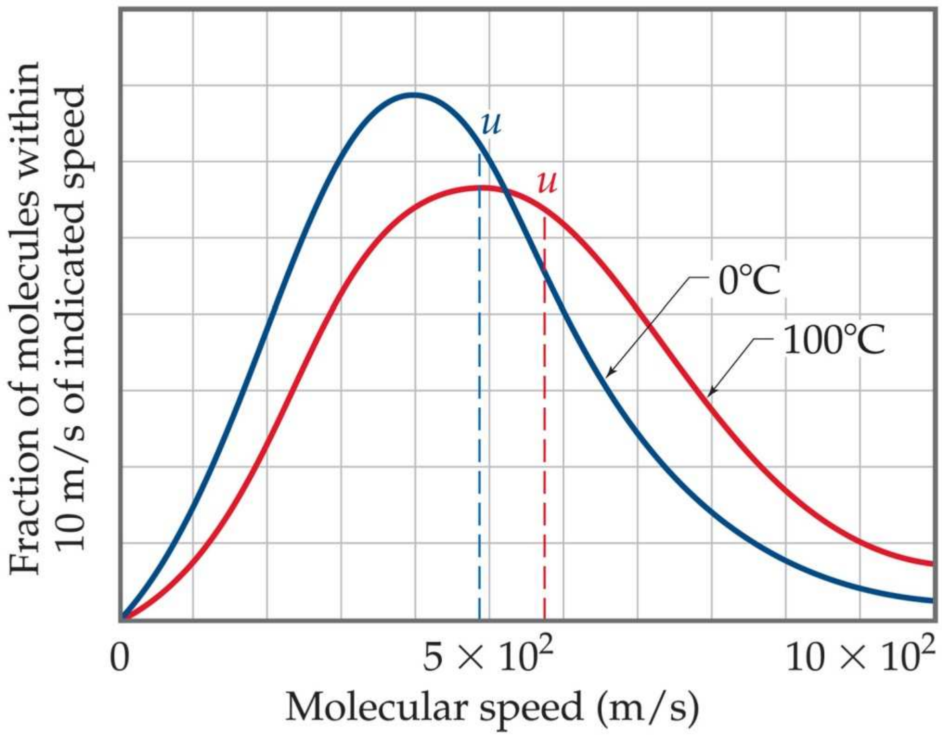
Main Tenets of Kinetic-Molecular Theory

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.

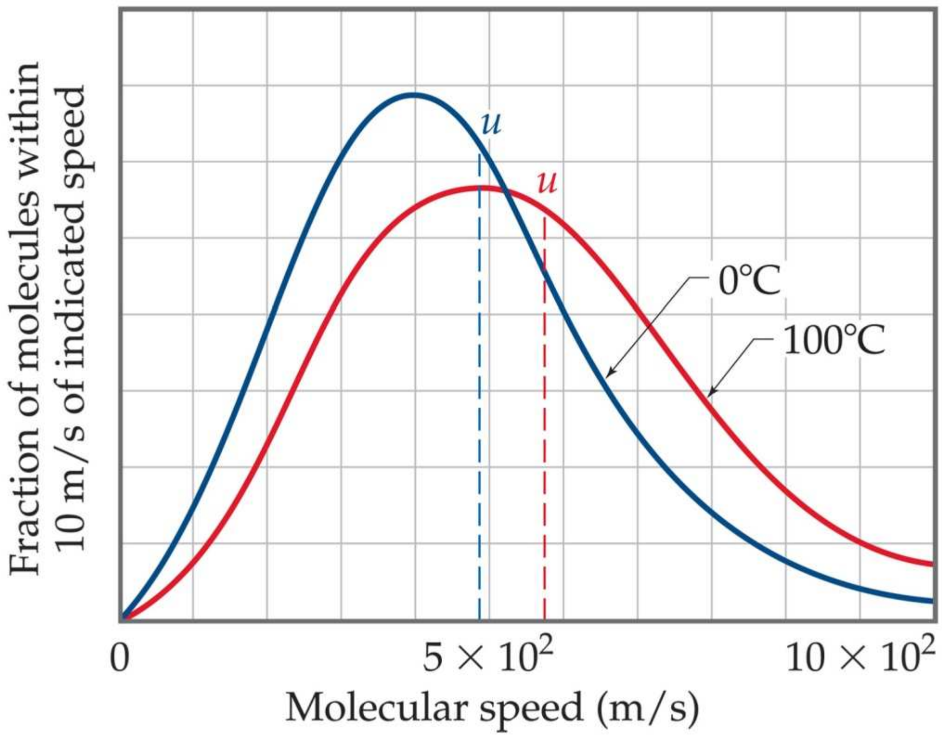
Main Tenets of Kinetic-Molecular Theory

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

- The pressure of the gas is caused by the collision of the molecules with the walls of the cylinder. The magnitude of the pressure depends on the frequency and the force of the collisions.
- The temperature of the gas depends on the average kinetic energy of the molecules.



- At higher temperatures a large fraction of molecules move at a greater speed.



- Root mean square (rms) speed.

$$\sqrt{\frac{1}{4}\left(4.0^2+6.0^2+10.0^2+12.0^2\right)}=\sqrt{74.0}=8.6m/s$$

- Average speed

$$\frac{1}{4}\left(4.0\ \ +6.0\ \ +10.0\ \ +12.0\ \ \right)=8.0m/s$$

- The average kinetic energy related to the rms

$$\varepsilon = \frac{1}{2} m v^2$$

- As KE increases with temperature, so does the rms speed (and of course the average speed)

Application to the gas law

Effect of *volume increase* at constant T

- KE is constant
- rms will remain constant
- If V increases the volume travels a longer distance between collisions
- This results in fewer collisions and hence lower pressure.

This is Boyles Law

$V \propto 1/P$

Effect of T increase at constant volume

- KE increases
- rms increases
- More collisions
- Hence higher pressure

Molecular Effusion and Diffusion

- The KE of any gas particle is a specific value at any given temperature
- It does not matter what the identity of the gas particle is, its energy would still be the same value
- But as KE = ½ MV^2

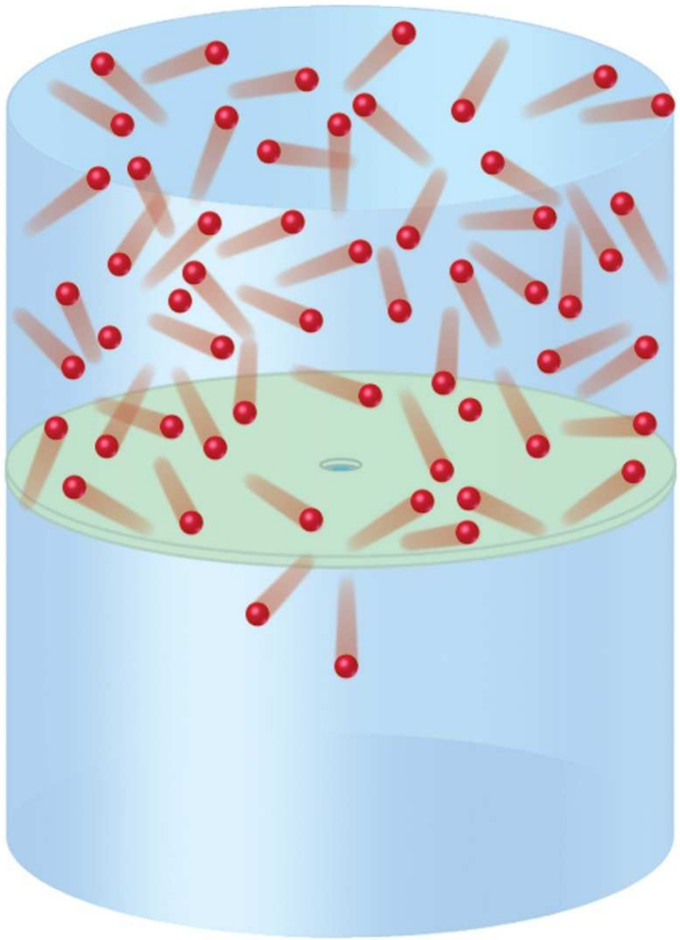
In such a case the particle with the higher mass would have lower rms speed.

The following equation expresses the relationship between the rms speed and the molar mass of the particles of gas

$$u = \sqrt{\frac{3RT}{M}}$$

(we will not be doing the derivation of this equation)

Effusion



The escape of gas molecules through a tiny hole into an evacuated space.

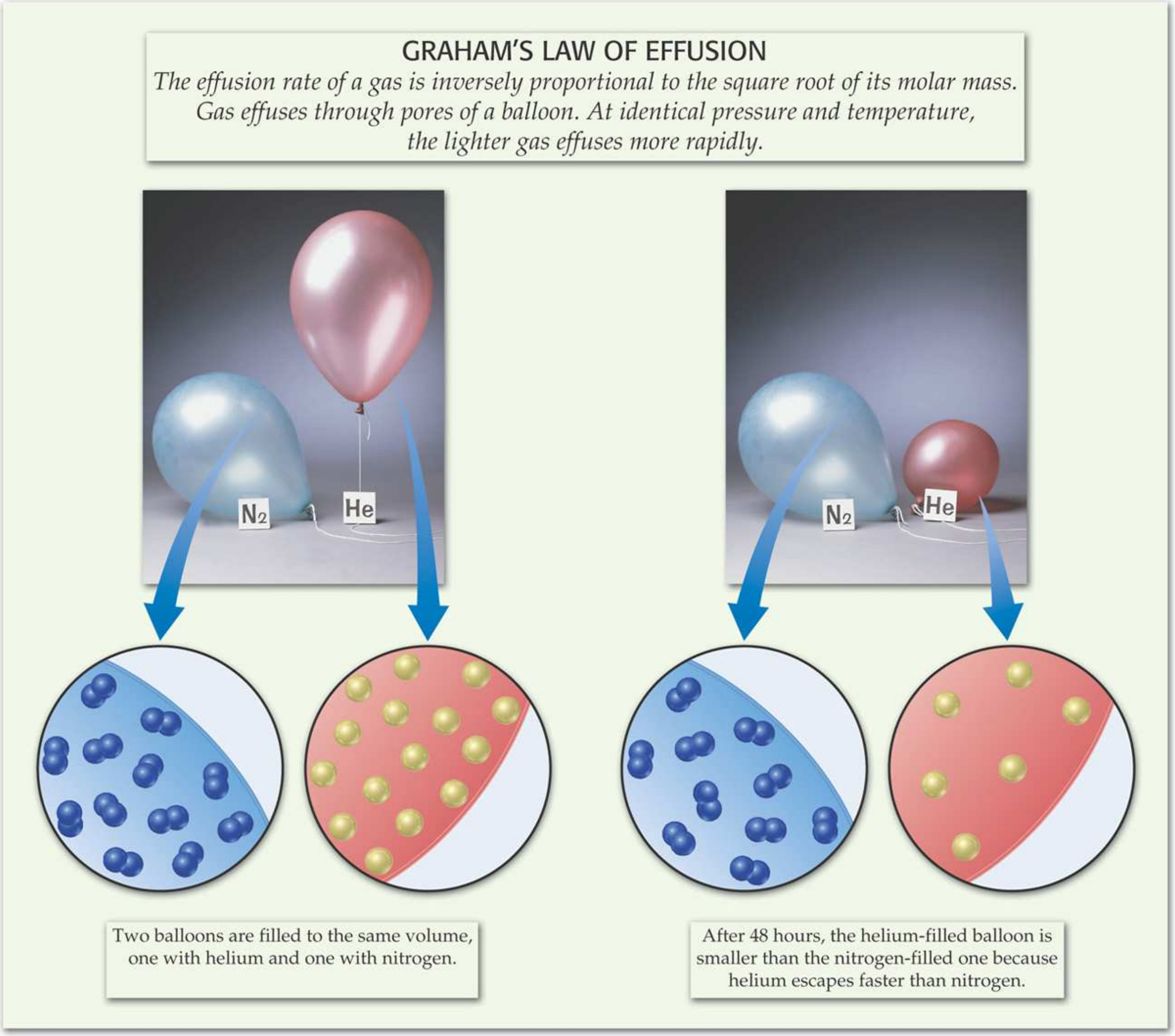
Diffusion

The spread of one substance throughout a space or throughout a second substance.

- Rate of effusion is directly proportionate to the rms speed of the molecule.

$$r \propto u$$

$$\frac{r1}{r2} = \frac{u1}{u2}$$


GRAHAM'S LAW OF EFFUSION
The effusion rate of a gas is inversely proportional to the square root of its molar mass. Gas effuses through pores of a balloon. At identical pressure and temperature, the lighter gas effuses more rapidly.
N2
He
N2
He
Two balloons are filled to the same volume, one with helium and one with nitrogen.
After 48 hours, the helium-filled balloon is smaller than the nitrogen-filled one because helium escapes faster than nitrogen.

10.15

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.

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

From the information given,

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

Thus,

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

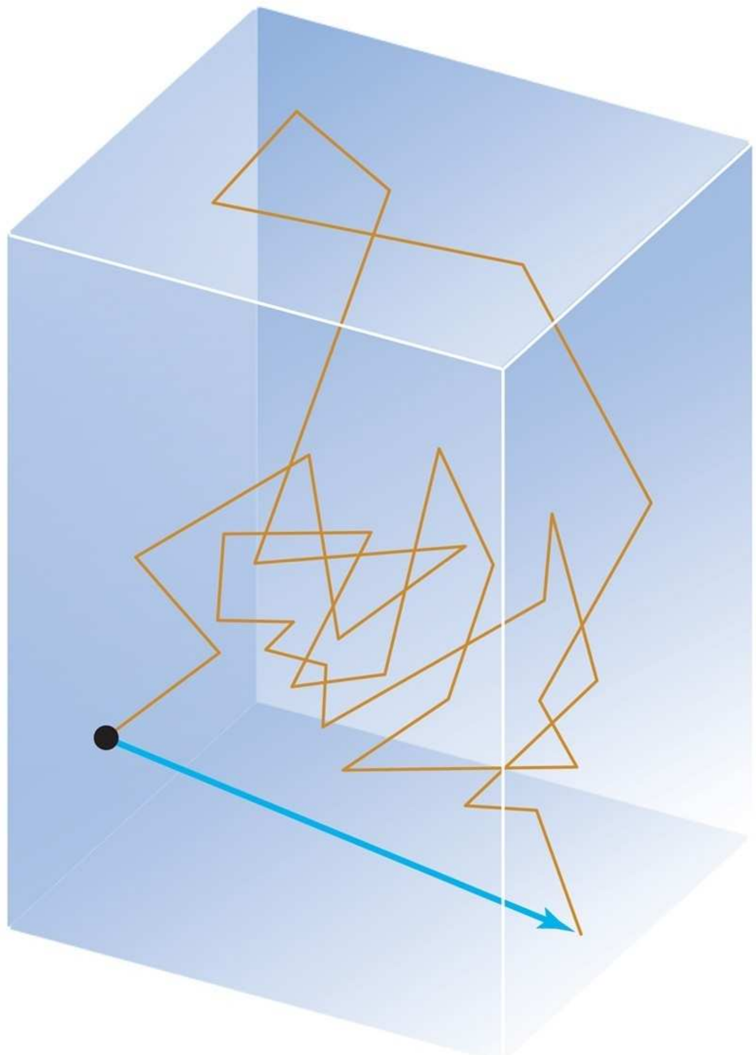
We now solve for the unknown molar mass, $\mathcal{M}_x$.

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

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

Diffusion and Mean Free Path

- Diffusion like effusion is faster for lower mass molecules.
- Molecular collision makes diffusion more complicated than effusion.
- Even though the speed of molecules at room temperature is very high, the molecules take a long time to diffuse because of the molecular collisions.



- Average distance traveled by a molecule between collisions is called the **<u>mean free path.</u>**
- The mean free path of air molecules at sea levels is 60nm and at about 100km altitude it is 10 cm

Real Gases: Deviation from Ideal Behavior

$PV = nRT$

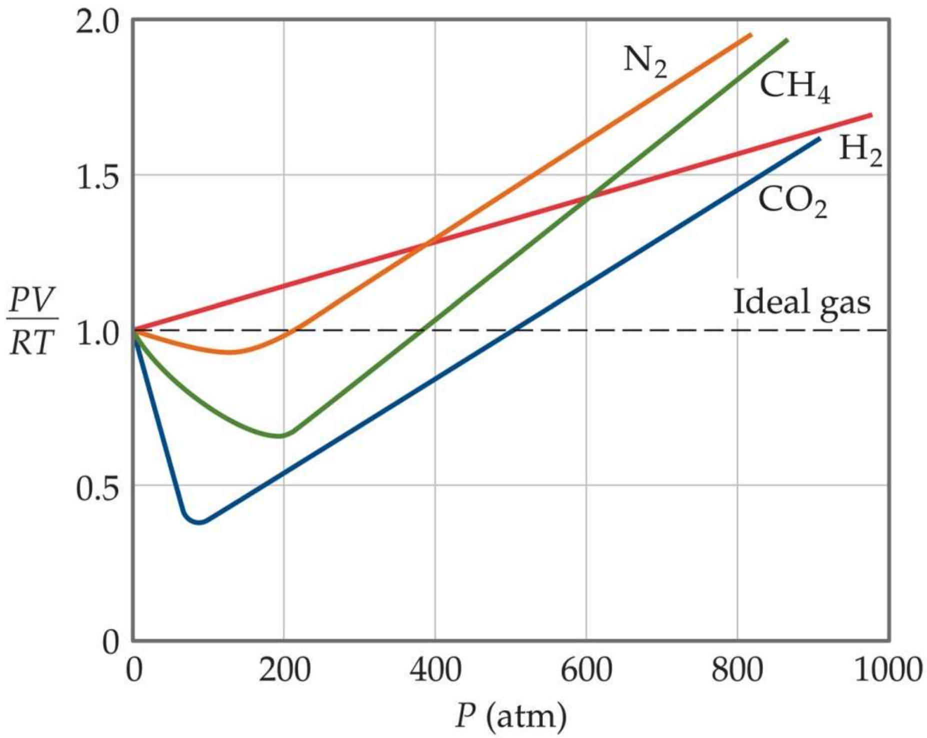
$$n = \frac{PV}{RT}$$

- For one mole of gas at any pressure

$$\frac{PV}{RT} = n = 1$$

The value of PV/RT is one for one mole of gas

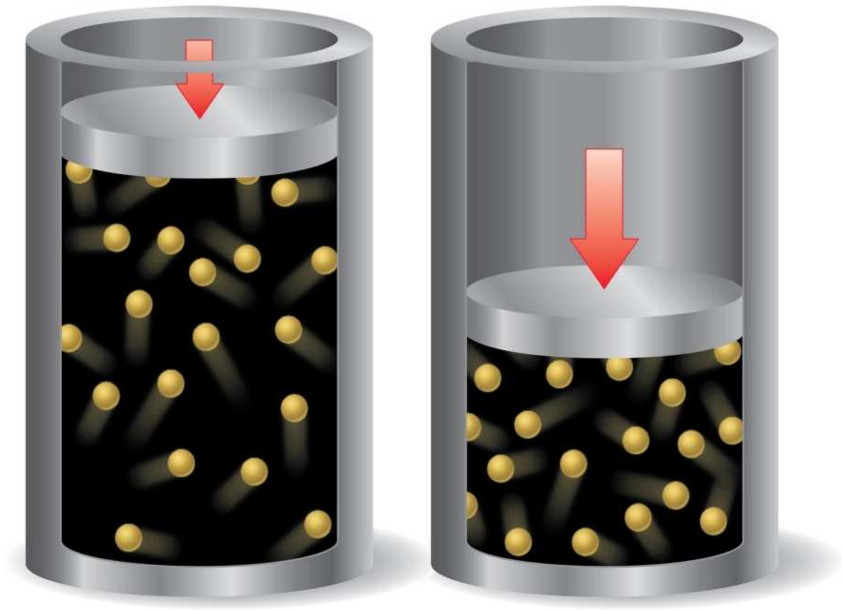
Real Gases

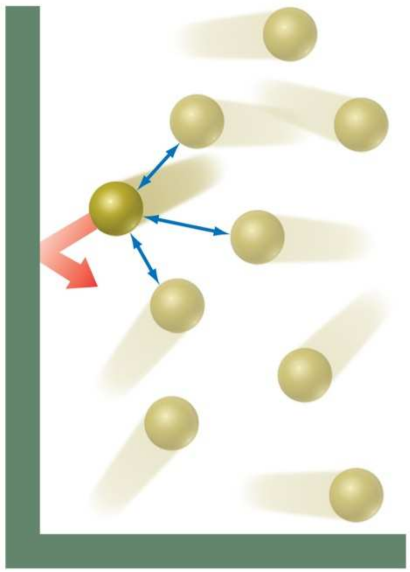


In the real world, the behavior of gases only conforms to the ideal-gas equation at relatively high temperature and low pressure.

- The real gases do have some volume and have some attraction for one another
- At high pressure the volume of the gas molecules becomes significant and the attractive forces come into play
- At low temperature the molecules are deprived of the energy they need to overcome their mutual attraction

Deviations from Ideal Behavior





The assumptions made in the kinetic-molecular model break down at high pressure and/or low temperature.

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 Waal Equation

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

$\frac{n^2a}{V^2}$

correction for the attractive forces between molecules, as the attractive force between the molecules reduces the overall pressure.

nb

the correction for volume of 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

- Larger molecules not only have larger volumes, they also have greater intermolecular attractive forces.

10.16 If 1.000 mol of an ideal gas were confined to 22.41 L at 0.0℃, 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℃.

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

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

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

- Homework question:

10.122 (11th edition).