Chapter 10
Gases

10.1 Characteristics of Gases

Characteristics of Gases

- Physical properties of gases are all similar.
- Composed mainly of nonmetallic elements with simple formulas and low molar masses.
- Unlike liquids and solids, gases
  - expand to fill their containers.
  - are highly compressible.
  - have extremely low densities.
- Two or more gases form a homogeneous mixture.

10.2 Pressure

Properties Which Define the State of a Gas Sample

1) Temperature
2) Pressure
3) Volume
4) Amount of gas, usually expressed as number of moles

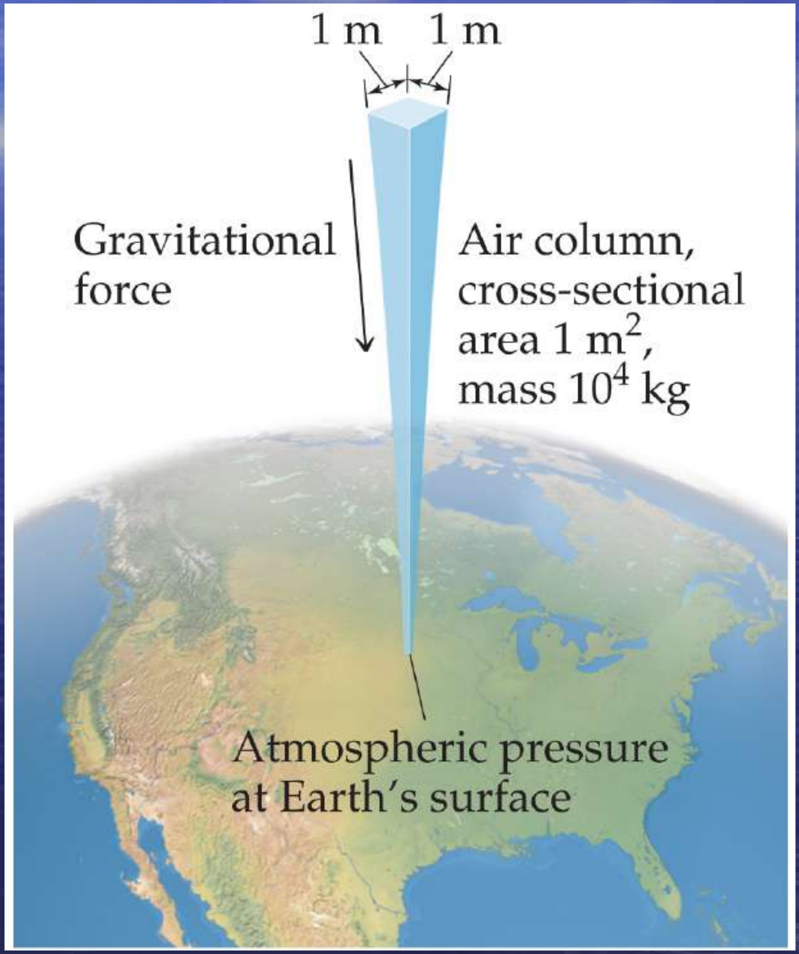
- Having already discussed three of these, we need to define pressure.

Pressure

- **Pressure** is the amount of force applied to an area:

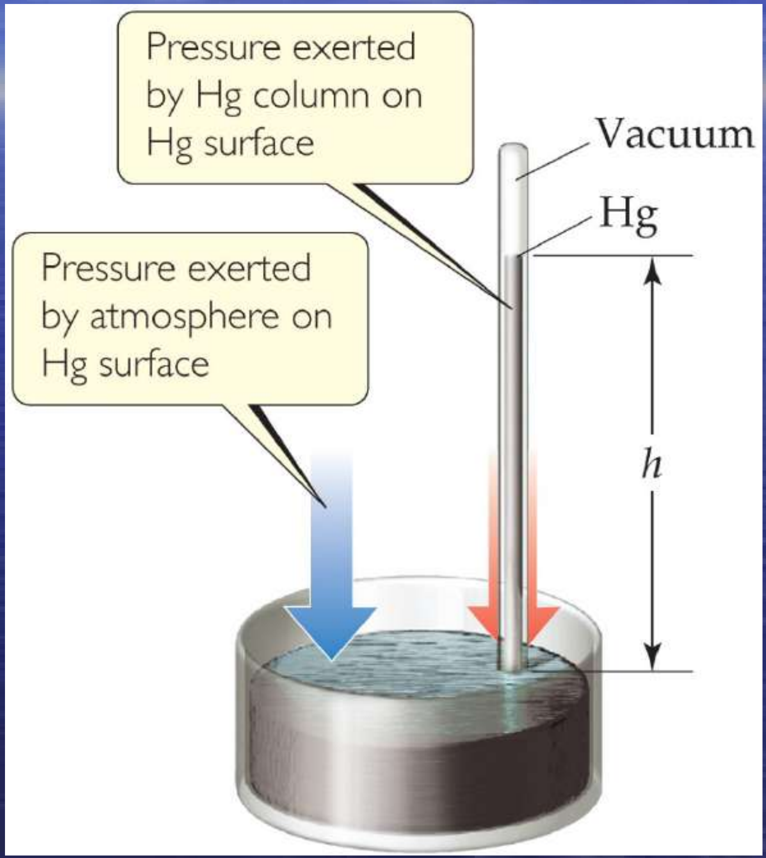
$$P = \frac{F}{A}$$

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



Units of Pressure

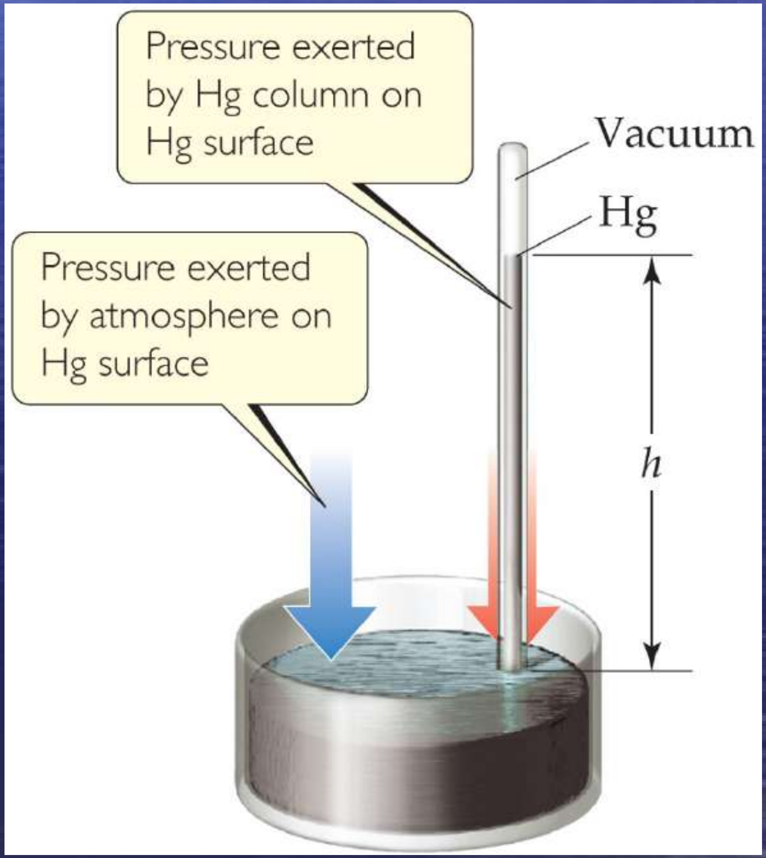
- **Pascals**: 1 Pa = 1 N/m^2 (SI unit of pressure)
- **Bar**: 1 bar = 10^5 Pa = 100 kPa
- **mm Hg or torr**: These units are literally the difference in the heights measured in mm of two connected columns of mercury, as in the **barometer** in the figure.
- **Atmosphere**:
- 1.00 atm = 760 torr = 760 mm Hg = 101.325 kPa



What happens to *h*, the height of the mercury column, if the atmospheric pressure increases?

a. Increases

b. Decreases



10.2 Give It Some Thought

Convert a pressure of 745 torr to units of

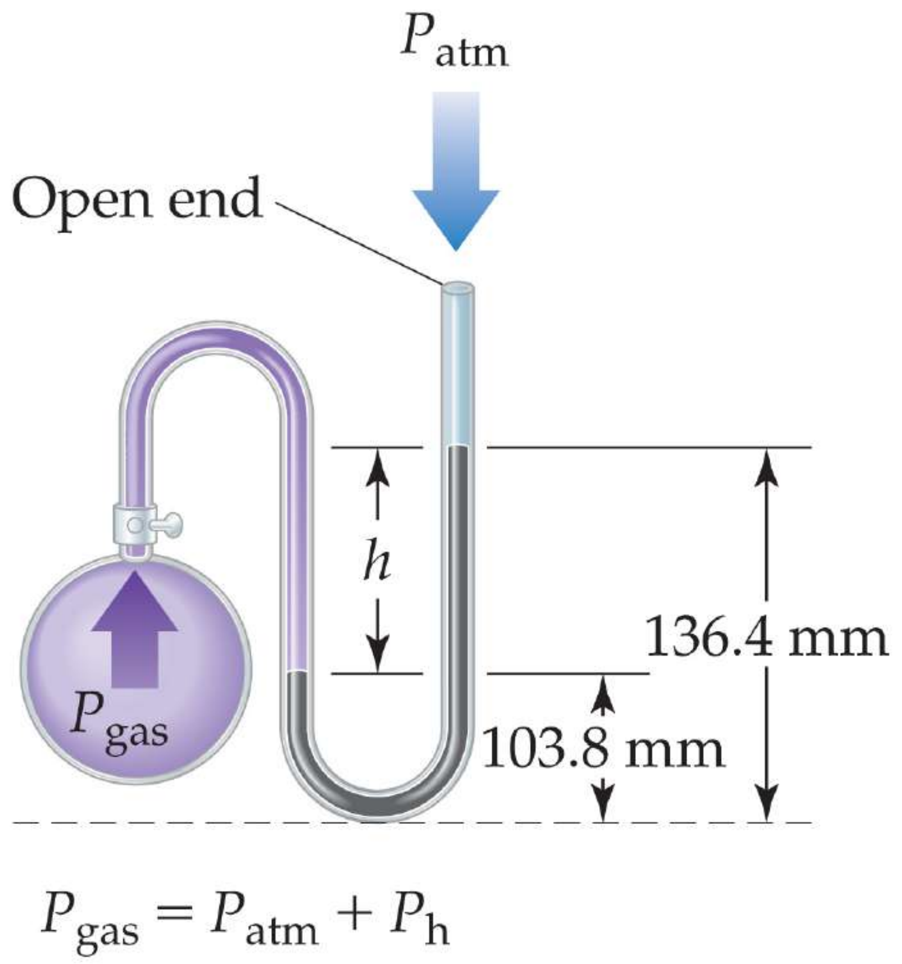
a) mmHg

b) atm

c) kPa

d) bar

Manometer



The **manometer** is used to measure the difference in pressure between atmospheric pressure and that of a gas in a vessel. (The barometer seen on the last slide is used to measure the pressure in the atmosphere at any given time.)

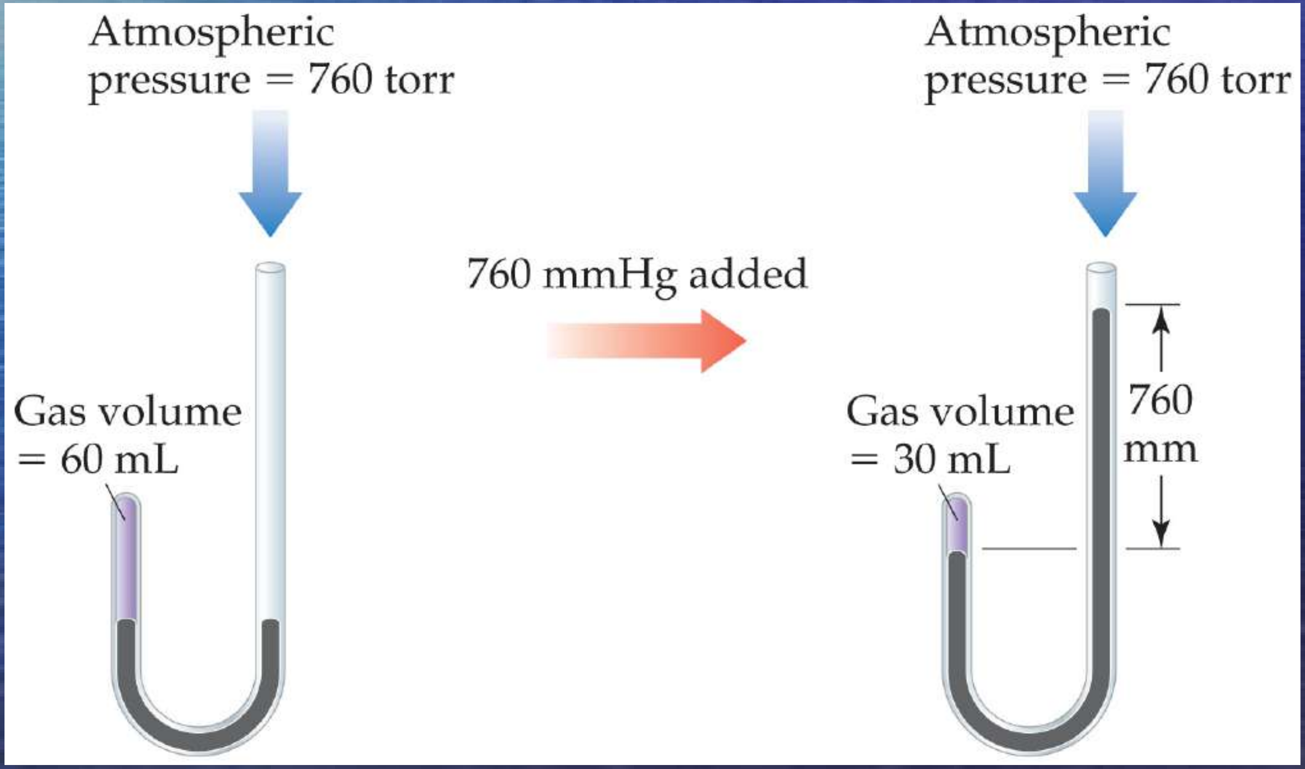
Sample Exercise 10.2

- On a certain day, the laboratory barometer reads 764.7 torr. A sample of gas is placed in a flask attached to an open-end mercury manometer. Using a meter stick, the level of mercury in the open-end 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 in atm and in kPa?

10.3 The Gas Laws

Boyle's Law

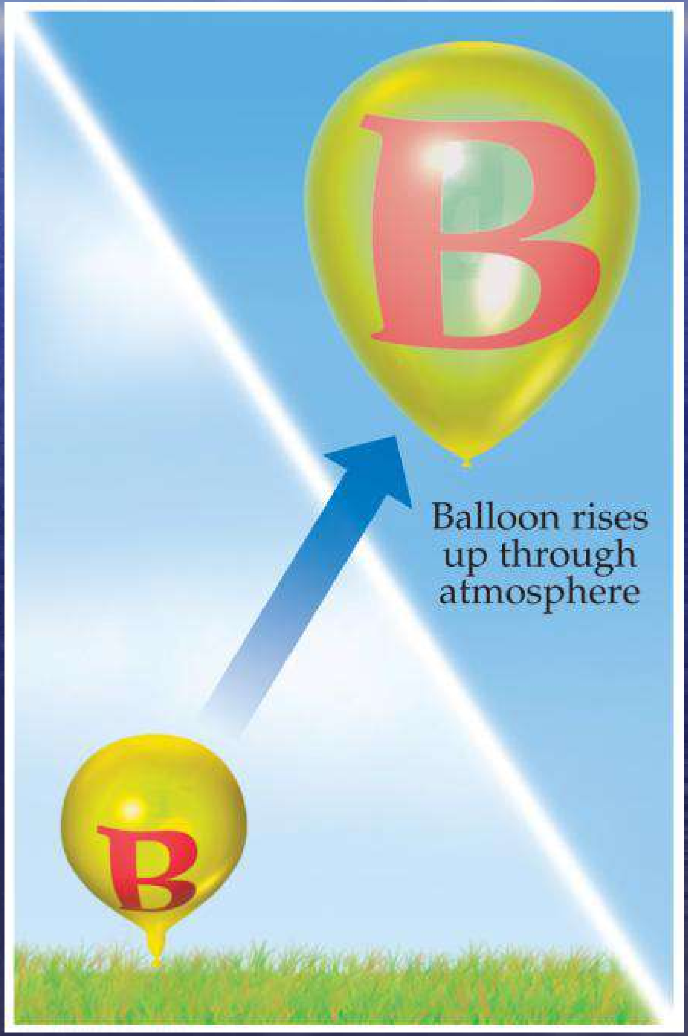
The volume of a fixed quantity of gas at constant temperature is inversely proportional to the pressure.



Does atmospheric pressure increase or decrease as altitude increases? (Neglect changes in temperature.)

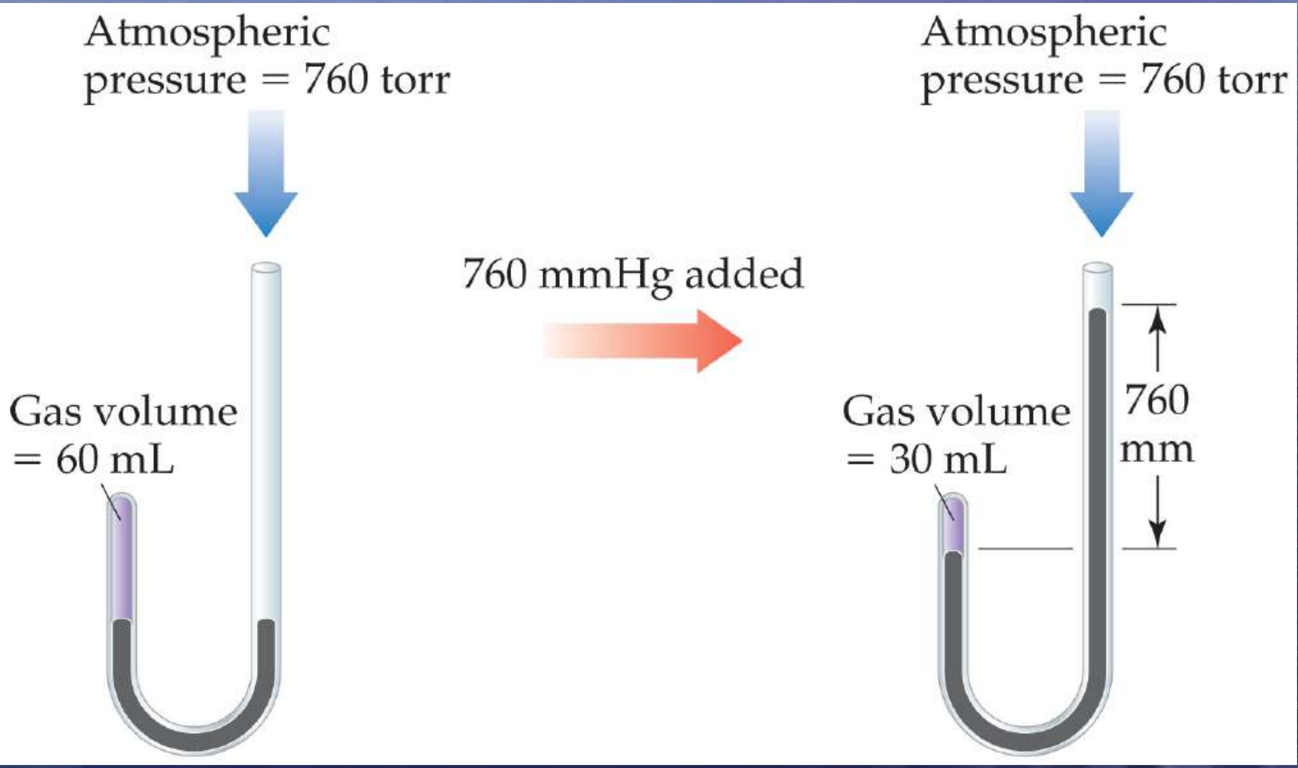
a. Increases

b. Decreases



What is the total pressure on the gas after the 760 mm Hg has been added?

a. 0 torr
b. 760 torr
c. 1140 torr
d. 1520 torr

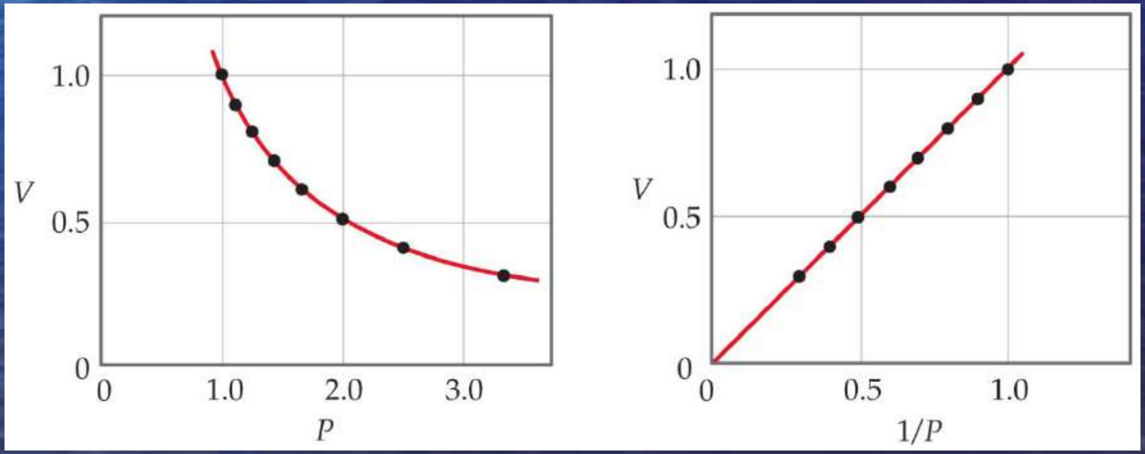


What happens to the pressure of a gas in a closed container if you double its volume while its temperature is held constant?

a. Increases by doubling its original value
b. Increases by tripling its original value
c. Decreases to half of its original value
d. Decreases to a fourth of its original value

Mathematical Relationships of Boyle's Law

- PV = a constant
- This means, if we compare two conditions: $P_1 V_1 = P_2 V_2$.
- Also, if we make a graph of V vs. P, it will *not* be linear. However, a graph of V vs. $1/P$ *will* result in a linear relationship!



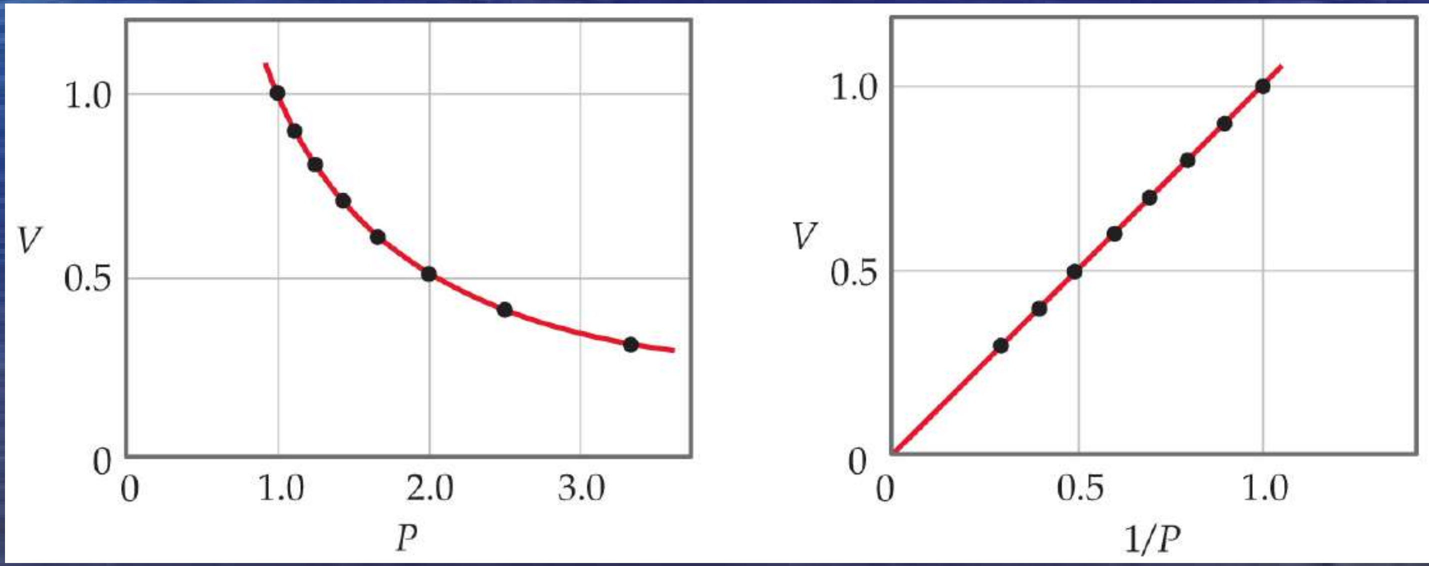
What would a plot of *P* versus 1/*V* look like for a fixed quantity of gas at a fixed temperature?

a. Polynomial curve of third order

b. Quadratic

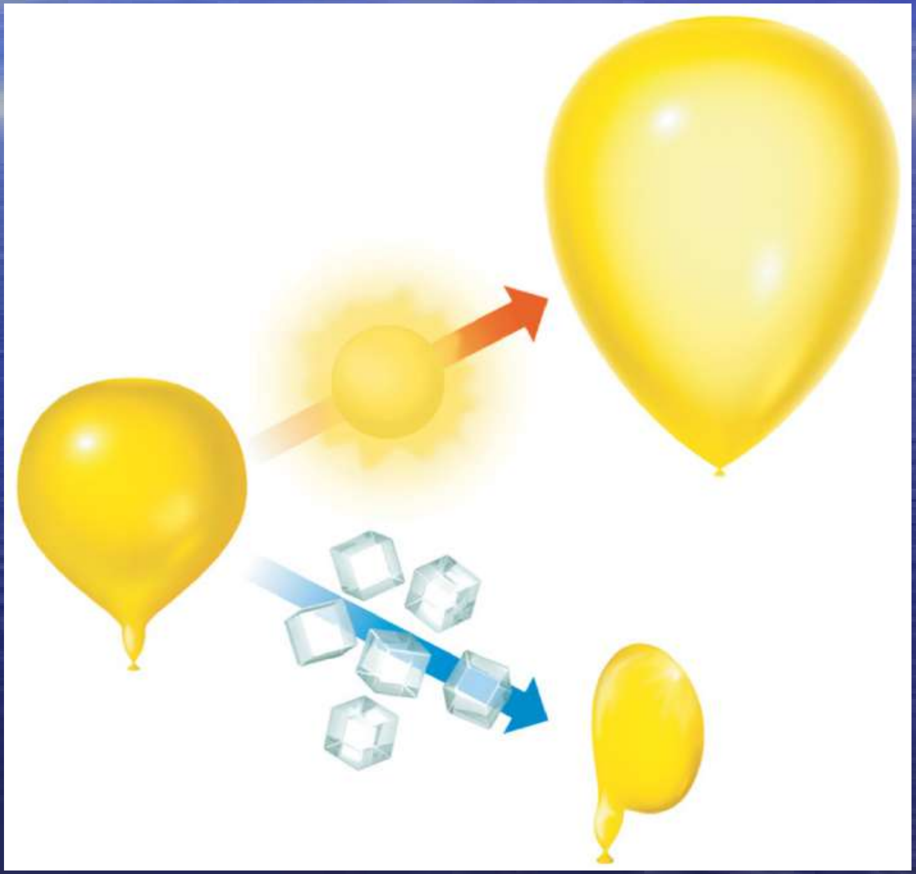
c. Exponential

d. Linear



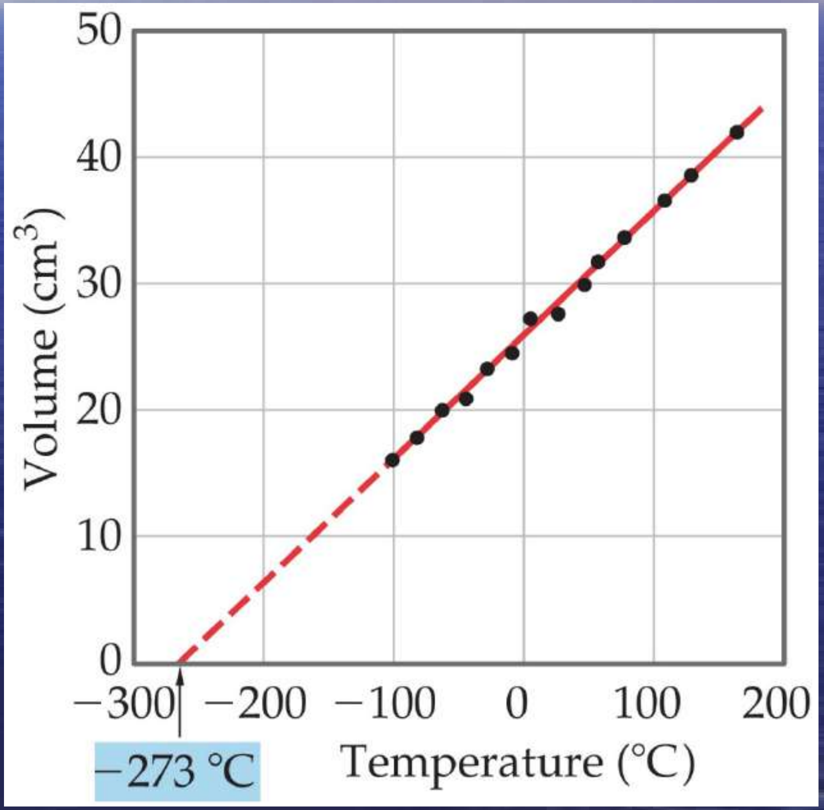
Charles's Law

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



Mathematical Relationships of Charles's Law

- $V = \text{constant} \times T$
- This means, if we compare two conditions: $V_1/T_1 = V_2/T_2$.
- Also, if we make a graph of V vs. T, it will be linear.



Does the volume of a fixed quantity of gas decrease to half its original value when the temperature is lowered from 100 °C to 50 °C?

a. Yes, because the temperature decreases by half.
b. No, because the temperature in kelvin (K) does not decrease by half.

Avogadro's Law

- The volume of a gas at constant temperature and pressure is directly proportional to the number of moles of the gas.
- Also, at STP, one mole of gas occupies 22.4 L.
- Mathematically: $V = \text{constant} \times n$, or $V_1/n_1 = V_2/n_2$

	He	N_2	CH_4
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}

How many moles of gas are in each vessel?

a. 0.5

b. 1

c. 1.5

d. 2

	He	N_2	CH_4
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}

Sample Exercise 10.3

Suppose we have a gas confined to a cylinder with a movable piston that is sealed so there are no leaks. How will each of the following changes affect (i) the pressure of the gas, (ii) the number of moles of gas in the cylinder, (iii) the average distance between molecules:

(a) Heating the gas while maintaining a constant pressure; **(b)** Reducing the volume while maintaining a constant temperature; **(c)** Injecting additional gas while keeping the temperature and volume constant.

Practice Exercise 1

A helium balloon is filled to a volume of 5.60 liters at 25 °C. What will the volume of the balloon become if it is put into liquid nitrogen to lower the temperature of the helium to 77 K?

(a) 17 L
(b) 22 L
(c) 1.4 L
(d) 0.046 L
(e) 3.7 L

Practice Exercise 2

An oxygen cylinder used in a hospital contains 35.4 L of oxygen gas at a pressure of 149.6 atm. How much volume would the oxygen occupy if it were transferred to a container that maintained a pressure of 1.00 atm if the temperature remains constant?

10.4 The Ideal-Gas Equation

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

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

- Finally, to make it an equality, we use a constant of proportionality (*R*) and reorganize; this gives the Ideal-Gas Equation: $PV = nRT$.

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

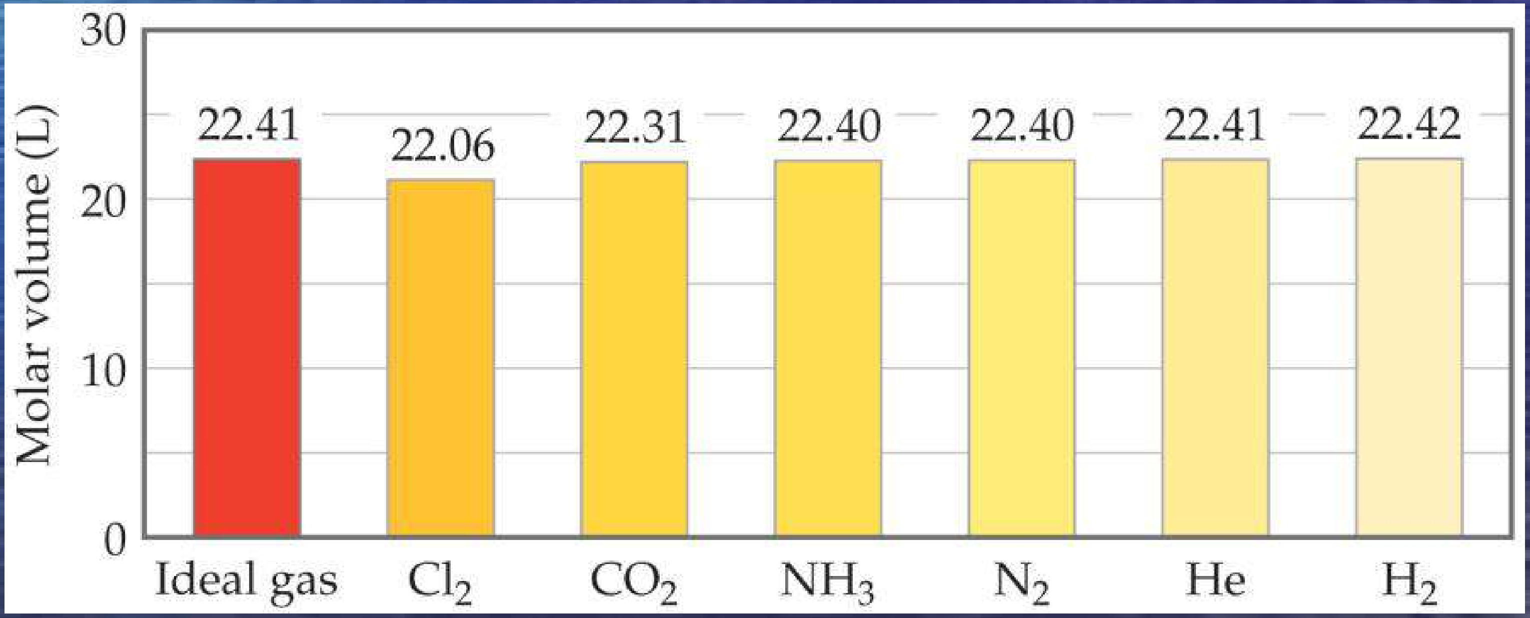
Which gas deviates most from ideal behavior?

a. Cl_2

b. CO_2

c. NH_3

d. H_2



If 1.00 mol of an ideal gas at STP were confined to a cube, what would be the length in cm of an edge of this cube?

a. $(22,410)^{1/3}$ cm
b. $(22.41)^{1/3}$ cm
c. $(2.241)^{1/3}$ cm
d. $(0.02241)^{1/3}$ cm

Sample Exercise 10.4

$CaCO_3$ decomposes upon heating to give CaO and CO_2. A sample of $CaCO_3$ is decomposed, and the CO_2 is collected in a 250 mL flask. After decomposition, the gas has a pressure of 1.3 atm at a temperature of 31ºC. How many moles of CO_2 gas were generated?

Practice Exercise 1

The Goodyear blimp contains 5.74×10^6 L of helium at 25 °C and 1.00 atm. What is the mass in grams of the helium inside the blimp?

(a) 2.30×10^7 g

(b) 2.80×10^6 g

(c) 1.12×10^7 g

(d) 2.34×10^5 g

(e) 9.39×10^5 g

Practice Exercise 2

Tennis balls are usually filled with either air or N_2 gas to a pressure above atmospheric pressure to increase their bounce. If a 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 °C?

Sample Exercise 10.5

The gas pressure in an aerosol can is 1.5 atm at 25ºC. What would the pressure be if the can were heated to 450ºC?

Practice Exercise 1

If you fill your car tire to a pressure of 32 psi (pounds per square inch) on a hot summer day when the temperature is 35 °C, what is the pressure (in psi) on a cold winter day when the temperature is –15 °C? **(a)** 38 psi

(b) 27 psi

(c) –13.7 psi

(d) 1.8 psi

(e) 13.7 psi.

Practice Exercise 2

The pressure in a natural-gas tank is maintained at 2.20 atm. On a day when the temperature is –15 °C, the volume of gas in the tank is 3.25×10^3 m^3. What is the volume of the same quantity of gas on a day when the temperature is 31 °C?

Sample Exercise 10.6

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. The temperature falls from 22ºC to -21ºC. Calculate the new volume of the balloon.

Practice Exercise 1

A gas occupies a volume of 0.75 L at 20 °C at 720 torr. What volume would the gas occupy at 41 °C and 760 torr?

(a) 1.45 L
(b) 0.85 L
(c) 0.76 L
(d) 0.66 L
(e) 0.35 L

Practice Exercise 2

A 0.50-mol sample of oxygen gas is confined at 0 °C and 1.0 atm in a cylinder with a movable piston. The piston compresses the gas so that the final volume is half the initial volume and the final pressure is 2.2 atm. What is the final temperature of the gas in degrees Celsius?

10.5 Further Applications of the Ideal-Gas Equation

Density of Gases

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

$$n/V = P/RT.$$

Also: moles × molecular mass = mass

$$n \times M = m.$$

If we multiply both sides by M, we get

$$m/V = MP/RT$$

and m/V is density, d; the result is:

$$d = MP/RT.$$

Density & Molar Mass of a Gas

To recap:

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

$d = MP/RT$

Also, if we know the mass, volume, and temperature of a gas, we can find its molar mass.

$M = mRT/PV$ or $M = dRT/P$

Is water vapor more or less dense than N_2 under the same conditions of temperature and pressure?

a. More dense

b. Less dense

Sample Exercise 10.7

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

Practice Exercise 1

What is the density of methane, CH_4, in a vessel where the pressure is 910 torr and the temperature is 255 K?

(a) 0.92 g/L
(b) 697 g/L
(c) 0.057 g/L
(d) 16 g/L
(e) 0.72 g/L

Practice Exercise 2

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.

Sample Exercise 10.8

A large flask is evacuated and found to weigh 134.567 g. It is then filled with gas to a pressure of 735 torr at 31ºC and reweighed; its mass is now 137.456 g. Finally, the flask is filled with water at 31ºC and found to weigh 1067.9 g. The density of water at this temperature is 0.997 g/mL. Calculate the molar mass of the unknown gas.

Practice Exercise 1

What is the molar mass of an unknown hydrocarbon whose density is measured to be 1.97 g/L at STP?

(a) 4.04 g/mol
(b) 30.7 g/mol
(c) 44.1 g/mol
(d) 48.2 g/mol

Practice Exercise 2

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.

Volume and Chemical Reactions

- The balanced equation tells us relative amounts of moles in a reaction, whether the compared materials are products or reactants.
- $PV = nRT$
- So, we can relate volume for gases, as well.
- For example: use ($PV = nRT$) for substance *A* to get moles *A*; use the mole ratio from the balanced equation to get moles *B*; and ($PV = nRT$) for substance *B* to get volume of *B*.

Sample Exercise 10.9

The air bags in automobiles are inflated by nitrogen gas produced from rapid decomposition of sodium azide, NaN_3.

$$2NaN_{3(s)} \rightarrow 2Na_{(s)} + 3N_{2(g)}$$

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

Practice Exercise 1

When silver oxide is heated, it decomposes according to the reaction below. If 5.76 g of Ag_2O is heated and the O_2 gas produced by the reaction is collected in an evacuated flask, what is the pressure of the O_2 gas if the volume of the flask is 0.65 L and the gas temperature is 25 °C?

$$2\,Ag_2O(s) \xrightarrow{\Delta} 4\,Ag(s) + O_2(g)$$

(a) 0.94 atm
(b) 0.039 atm
(c) 0.012 atm
(d) 0.47 atm
(e) 3.2 atm

Practice Exercise 2

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 ammonia at 850ºC and 5.00 atm are required to react with 1.00 mol of O_2 in this reaction?

10.6 Gas Mixtures and Partial Pressures

Dalton’s Law ofPartial Pressures

- If two gases that *don’t* react are combined in a container, they act as if they are alone in the container.
- 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,

$$P_{total} = p_1 + p_2 + p_3 + \ldots$$

How is the partial pressure exerted by N_2 gas affected when some O_2 is introduced into a container if the temperature and volume remain constant? How is the total pressure affected?

a. The partial pressure exerted by N_2 gas does not change when O_2 is added to the container; the total pressure increases.
b. The partial pressure exerted by N_2 gas changes only if an equal or greater amount of O_2 is added to the container; if that condition is met, the total pressure increases.
c. The partial pressure exerted by N_2 gas decreases when O_2 is added to the container; the total pressure remains the same.
d. The partial pressure exerted by N_2 gas increases when O_2 is added to the container; the total pressure remains the same.

Sample Exercise 10.10

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 0ºC. What is the partial pressure of each gas, and what is the total pressure in the vessel?

Practice Exercise 1

A 15-L cylinder contains 4.0 g of hydrogen and 28 g of nitrogen. If the temperature is 27 °C what is the total pressure of the mixture?

(a) 0.44 atm
(b) 1.6 atm
(c) 3.3 atm
(d) 4.9 atm
(e) 9.8 atm

Practice Exercise 2

What is the total pressure exerted by a mixture of 2.00 g of $H_2(g)$ and 8.00 g of $N_2(g)$ at 273 K in a 10.0-L vessel?

Mole Fraction

- Because each gas in a mixture acts as if it is alone, we can relate amount in a mixture to partial pressures:

$$\frac{P_1}{P_t} = \frac{n_1 RT/V}{n_t RT/V} = \frac{n_1}{n_t}$$

- That ratio of moles of a substance to total moles is called the **mole fraction**, χ.

$$X_1 = \frac{\text{Moles of compound 1}}{\text{Total moles}} = \frac{n_1}{n_t}$$

Pressure and Mole Fraction

- The end result is

$$P_1 = \left(\frac{n_1}{n_t}\right) P_t = X_1 P_t$$

Sample Exercise 10.11

A study of the effects of certain gases on plant growth requires a synthetic atmosphere composed of 1.5 mol % CO_2, 18.0 mol % O_2, and 80.5 mol % 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?

Practice Exercise 1

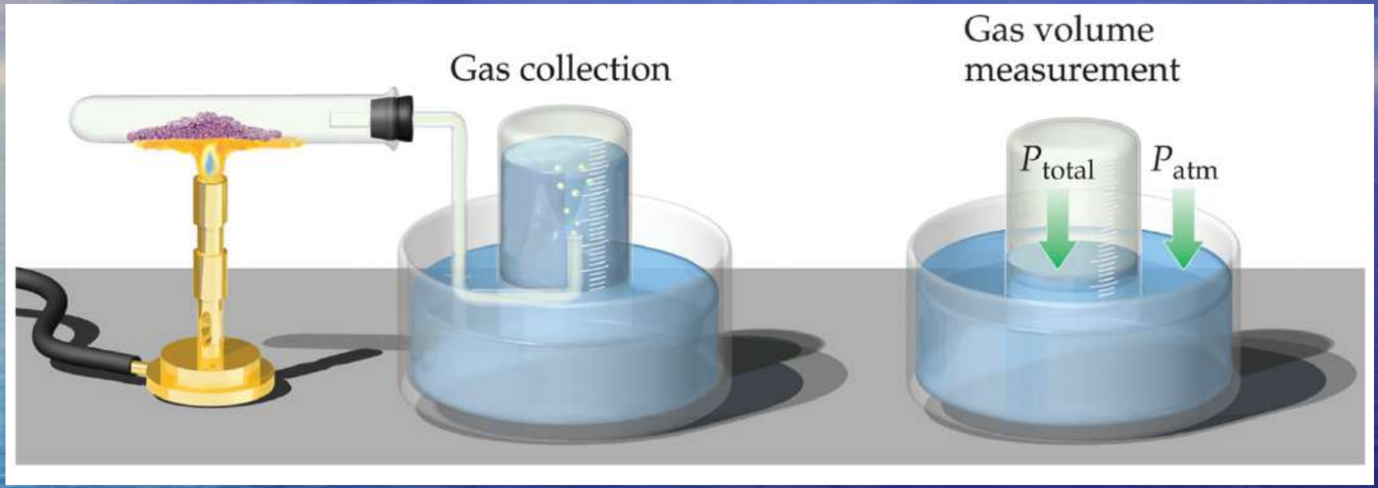
A 4.0-L vessel containing N_2 at STP and a 2.0-L vessel containing H_2 at STP are connected by a valve. If the valve is opened allowing the two gases to mix, what is the mole fraction of hydrogen in the mixture?

(a) 0.034
(b) 0.33
(c) 0.50
(d) 0.67
(e) 0.96

Practice Exercise 2

From data gathered by *Voyager 1*, scientists have estimated the composition of the atmosphere of Titan, Saturn's largest moon. The pressure on the surface of Titan is 1220 torr. The atmosphere consists of 82 mol % N_2, 12 mol % Ar, and 6.0 mol % CH_4. Calculate the partial pressure of each gas.

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.

Collecting Gas over Water Example Problem

A sample of $KClO_3$ is partially decomposed producing O_2 gas that is collected over water. The volume of the gas collected is 0.250 L at 26ºC and 765 torr total pressure.

- A) How many moles of O_2 are collected?
- B) How many grams of $KClO_3$ were decomposed?

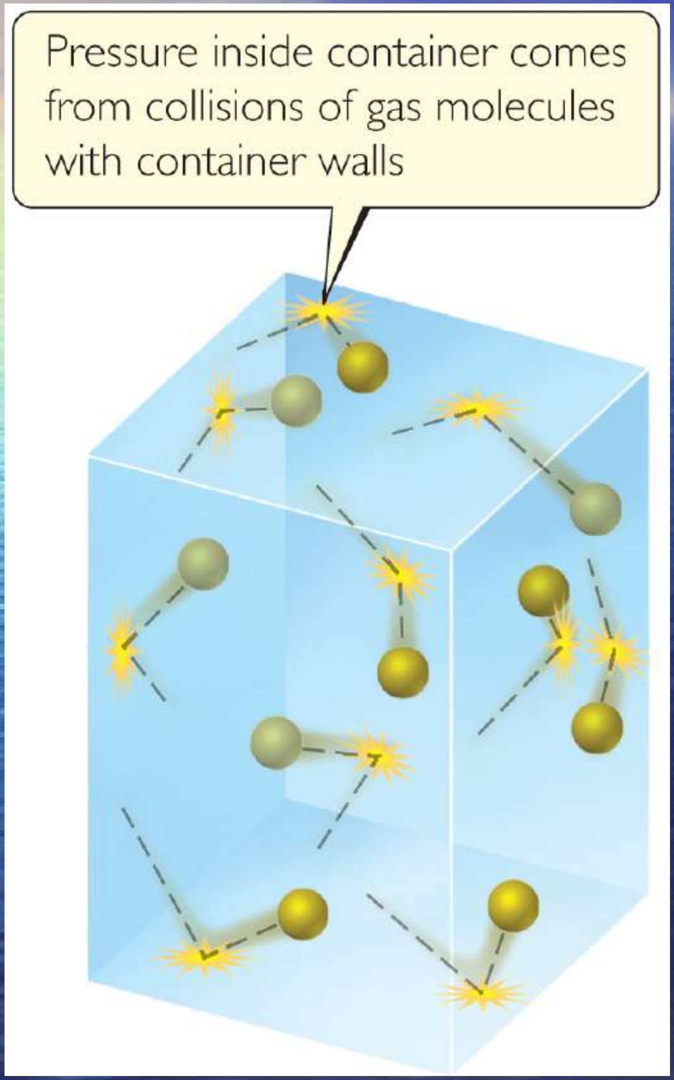
Collecting Gas Over Water Practice Problem

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

- $NH_4NO_{2(s)} \rightarrow N_{2(g)} + 2H_2O_{(l)}$
- When a sample of NH_4NO_2 is decomposed in a test tube, 511 mL of nitrogen gas is collected over water at 26ºC and 745 torr total pressure. How many grams of NH_4NO_2 were decomposed?

10.7 Kinetic-Molecular Theory

Kinetic-Molecular Theory

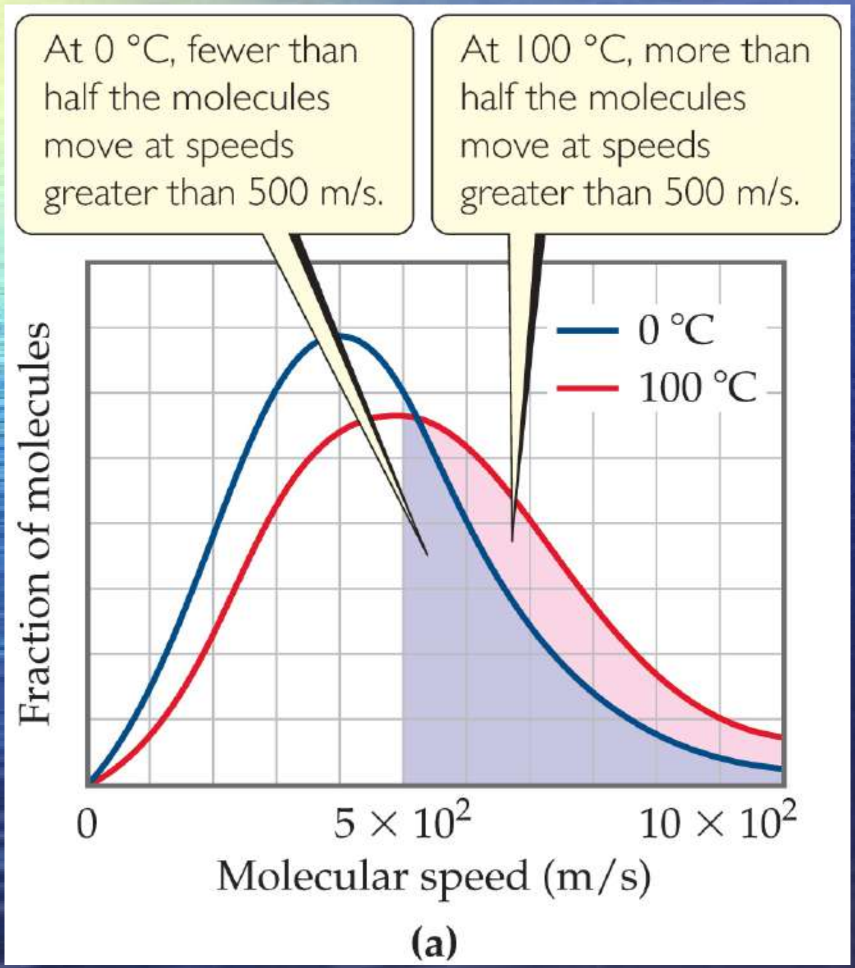


- *Laws* tell us *what* happens in nature. Each of the gas laws we have discussed tell us what is observed under certain conditions.
- *Why* are these laws observed? We will discuss a *theory* to explain our observations.

Main Tenets of Kinetic-Molecular Theory

1) Gases consist of large numbers of molecules that are in continuous, random motion.
2) The combined volume of all the molecules of the gas is negligible relative to the total volume in which the gas is contained.
3) Attractive and repulsive forces between gas molecules are negligible.

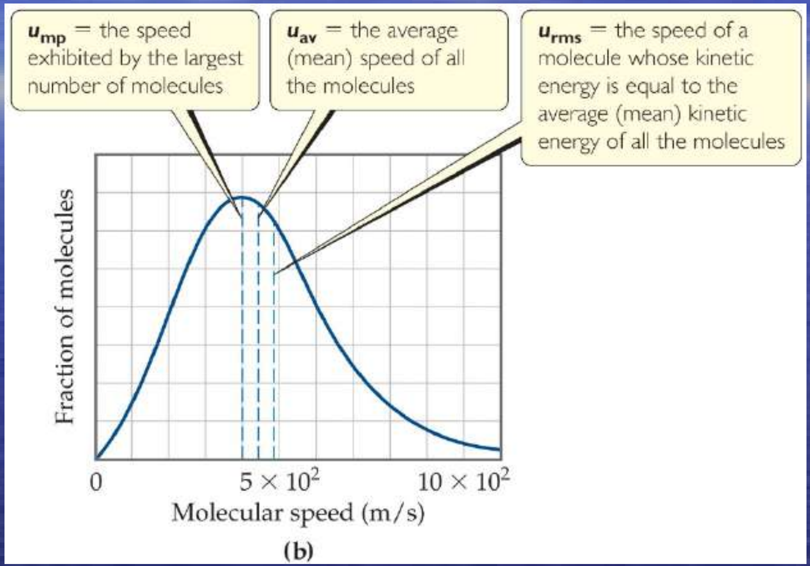
Main Tenets of Kinetic-Molecular Theory



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

How Fast Do Gas Molecules Move?

- Temperature is related to their *average* kinetic.
- Individual molecules can have different speeds of motion.
- The figure shows three different speeds:
- u_{mp} is the most probable speed (most molecules are this fast).
- u_{av} is the average speed of the molecules.
- u_{rms}, the root-mean-square speed, is the one associated with their average kinetic energy.



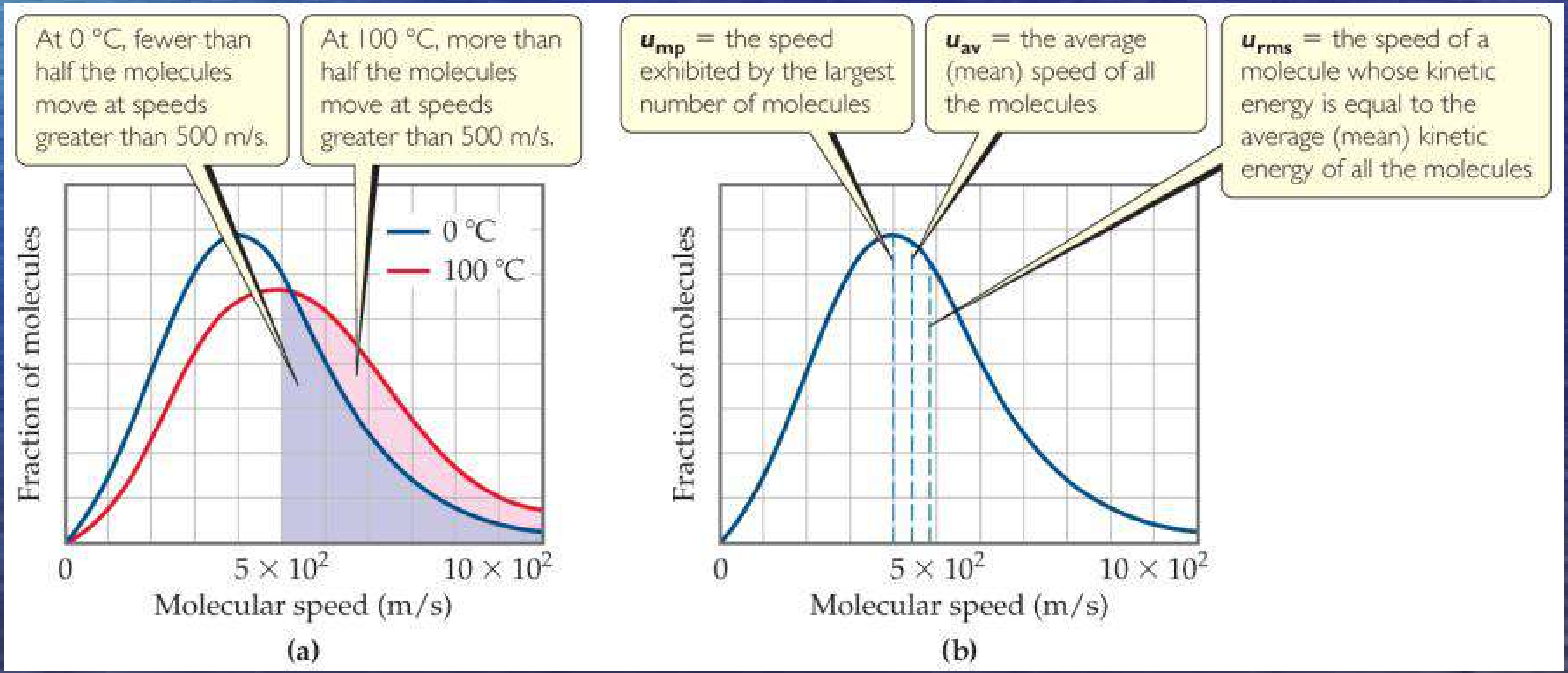
Estimate the fraction of molecules at 100 °C with speeds less than 300 m/s.

a. 1/10

b. 1/3

c. 1/2

d. 2/3



Consider three gases all at 298 K: HCl, H_2, and O_2. List the gases in order of increasing average speed.

a. Additional pressure information is needed to compare average speeds.
b. $HCl < O_2 < H_2$
c. $HCl < H_2 < O_2$
d. $H_2 < O_2 < HCl$

Sample Exercise 10.12

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 the molecules

(b) their average speed

(c) the number of collisions they make with the container walls per unit time

(d) the number of collisions they make with a unit area of container wall per unit time

(e) the pressure?

Practice Exercise 1

Consider two gas cylinders of the same volume and temperature, one containing 1.0 mol of propane, C_3H_8, and the other 2.0 mol of methane, CH_4. Which of the following statements is true?

(a) The C_3H_8 and CH_4 molecules have the same u_{rms}

(b) The C_3H_8 and CH_4 molecules have the same average kinetic energy

(c) The rate at which the molecules collide with the cylinder walls is the same for both cylinders

(d) The gas pressure is the same in both cylinders.

Practice Exercise 2

How is the rms speed of N_2 molecules in a gas changed by:

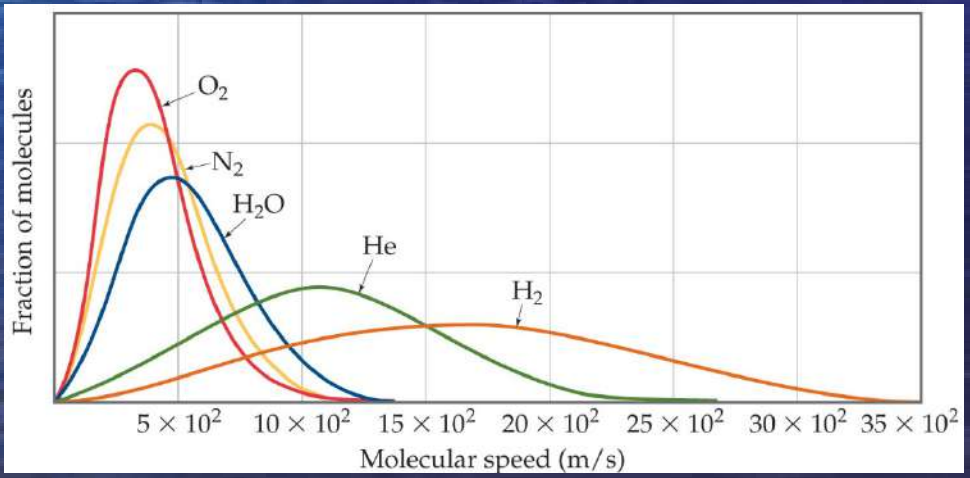
- A) An increase in temperature
- B) An increase in volume
- C) Mixing with a sample of Ar at the same temperature?

10.8 Molecular Effusion and Diffusion

u_{rms} and Molecular Mass

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

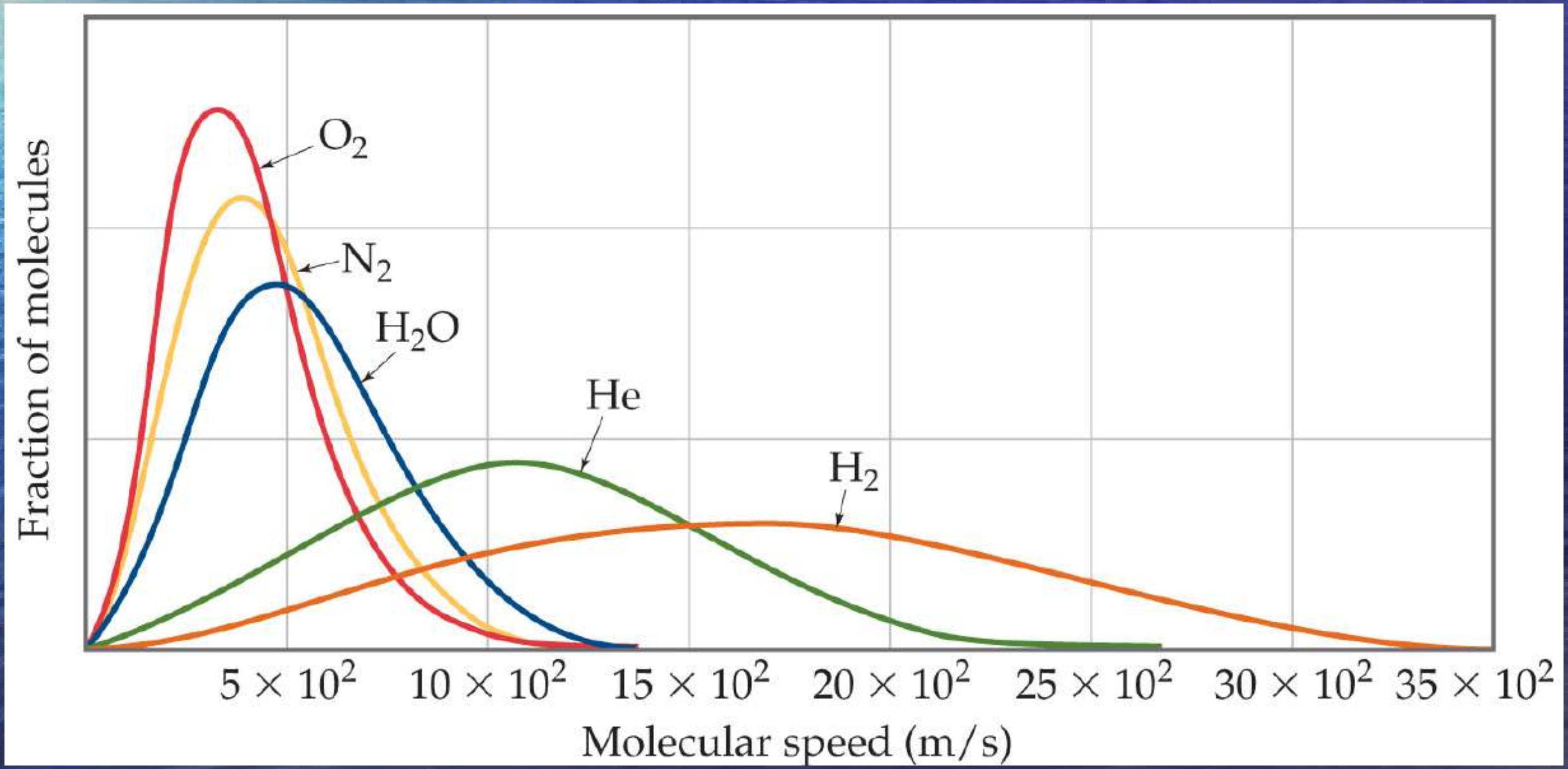
- At any given temperature, the average kinetic energy of molecules is the same.
- So, ½ m $(u_{rms})^2$ is the same for two gases at the same temperature.
- If a gas has a low mass, its speed will be greater than for a heavier molecule.



Which of these gases has the largest molar mass? Which has the smallest?

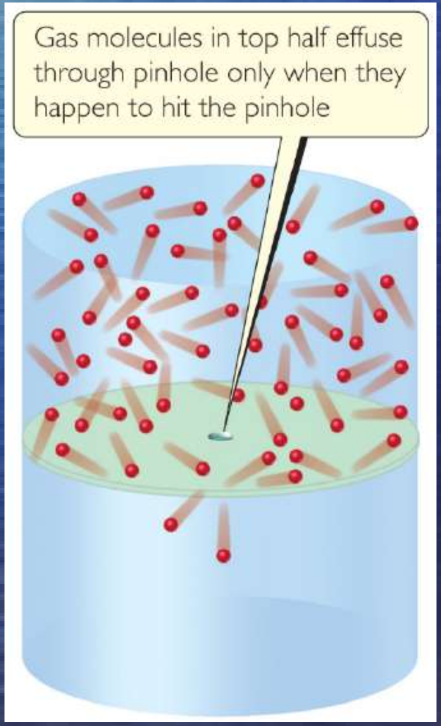
a. O_2; H_2

b. H_2; O_2

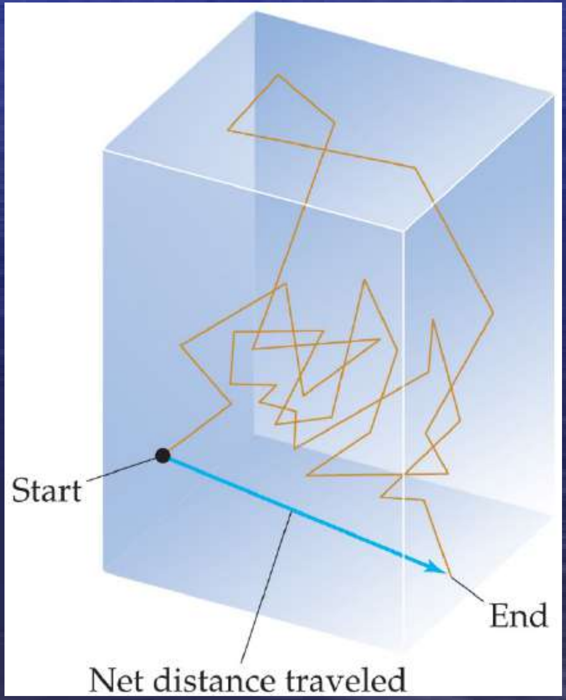


Effusion & Diffusion

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



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



Graham's Law Describes Diffusion & Effusion

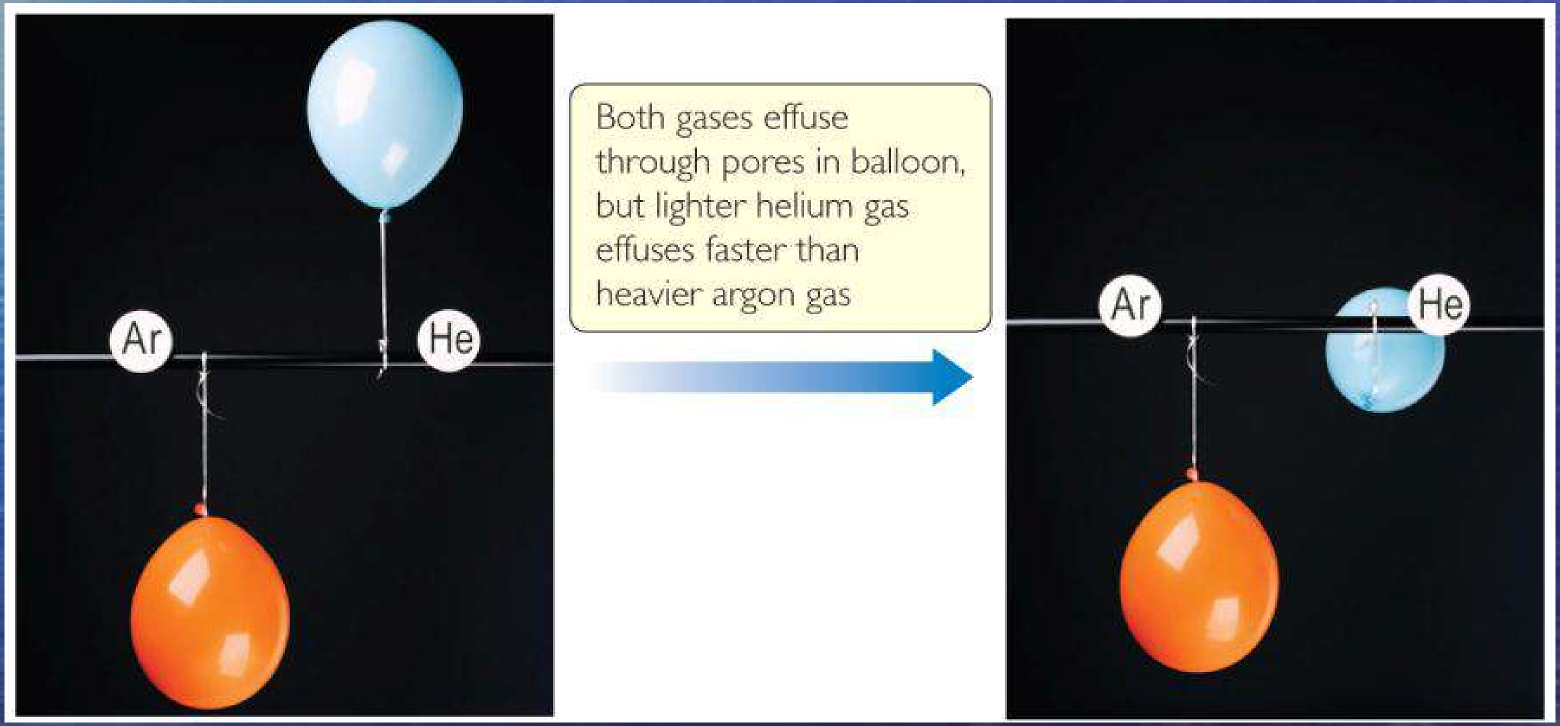
- Graham's Law relates the molar mass of two gases to their rate of speed of travel.
- The "lighter" gas always has a faster rate of speed.

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

Because pressure and temperature are constant in this figure but volume changes, which other quantity in the ideal-gas equation must also change?

a. R

b. *n*



Will these changes increase, decrease, or have no effect on the mean free path of the molecules in a gas sample?

(a) increasing pressure.

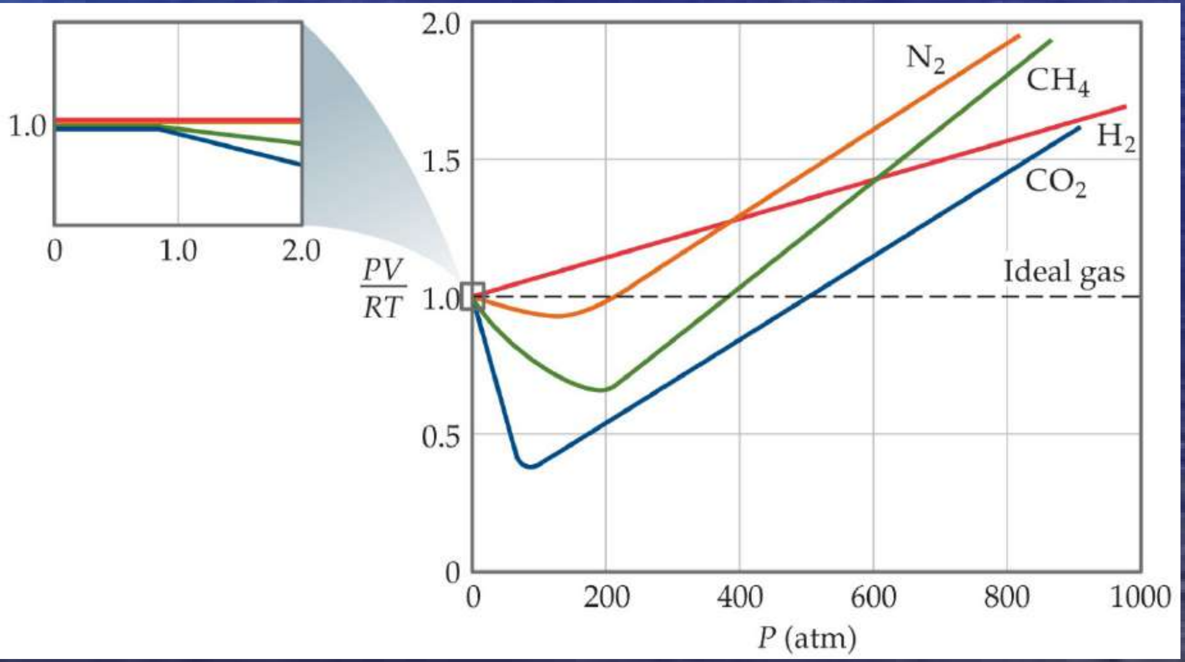
(b) increasing temperature.

	Increasing P	Increasing T
a.	Increase	Increase
b.	Decrease	No change
c.	Increase	Decrease
d.	No change	Decrease

10.9 Real Gases: Deviations from Ideal Behavior

Real Gases

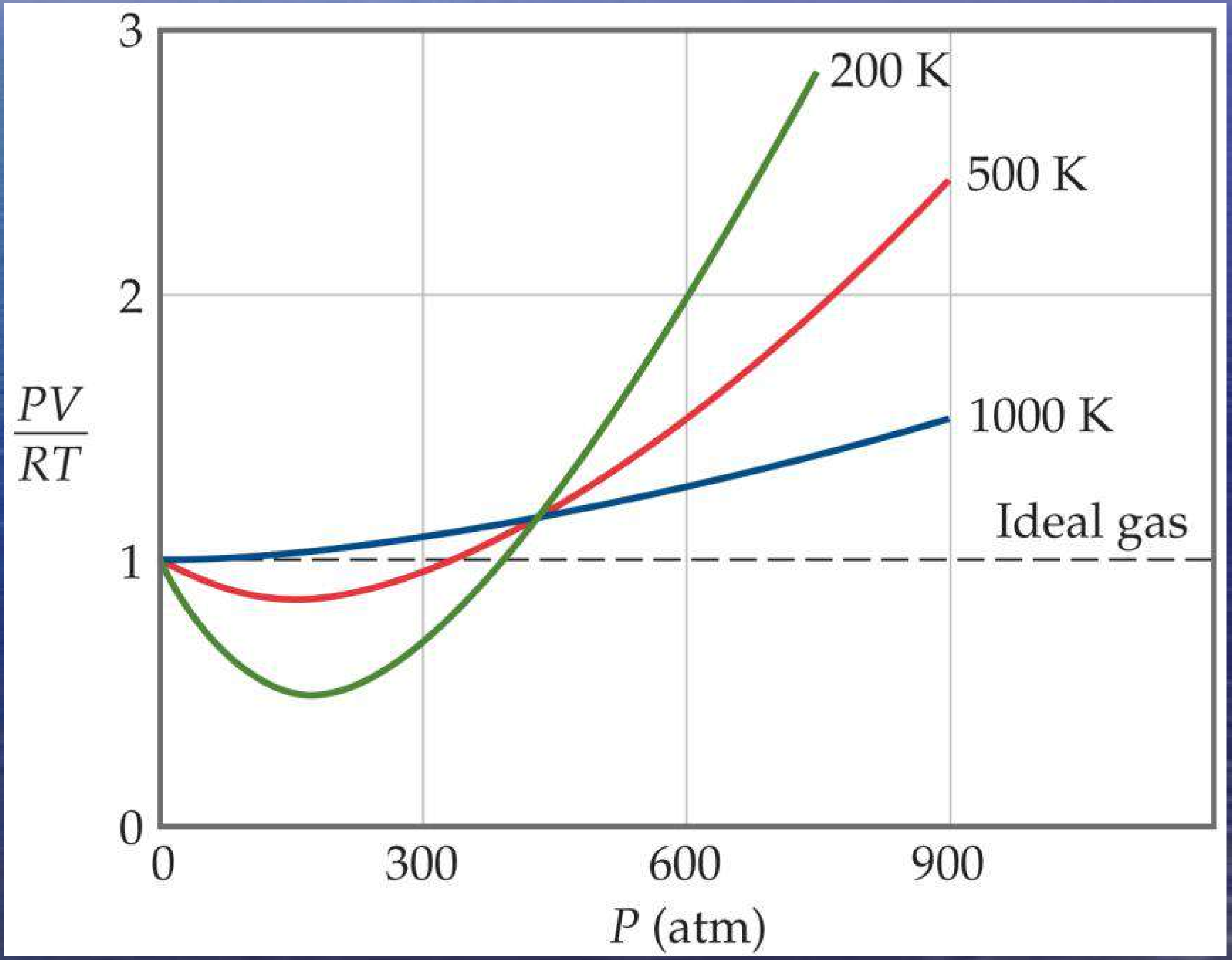
- In the real world, the behavior of gases only conforms to the ideal-gas equation at relatively high temperature and low pressure.
- Even the same gas will show wildly different behavior under high pressure at different temperatures.



True or false: Nitrogen gas behaves more like an ideal gas as the temperature increases.

a. True

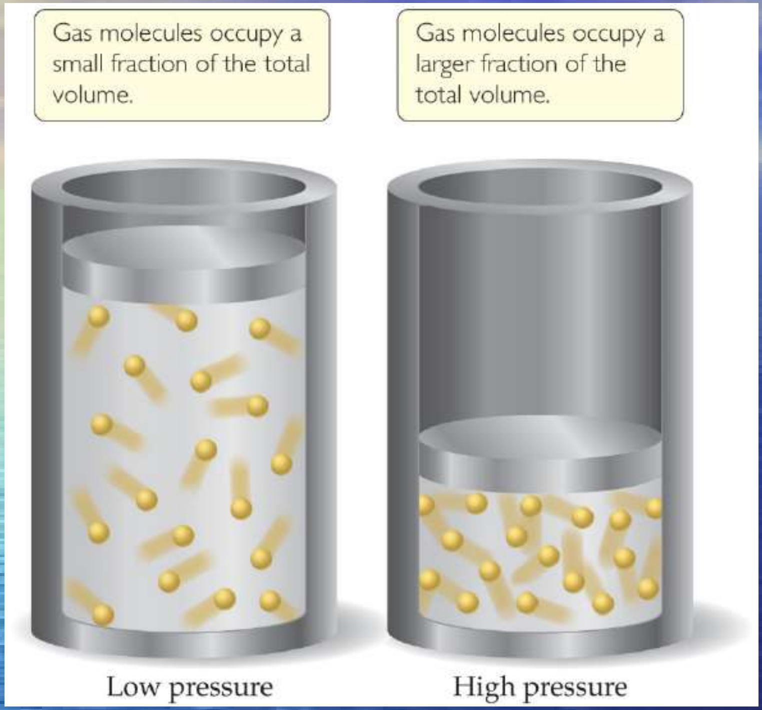
b. False

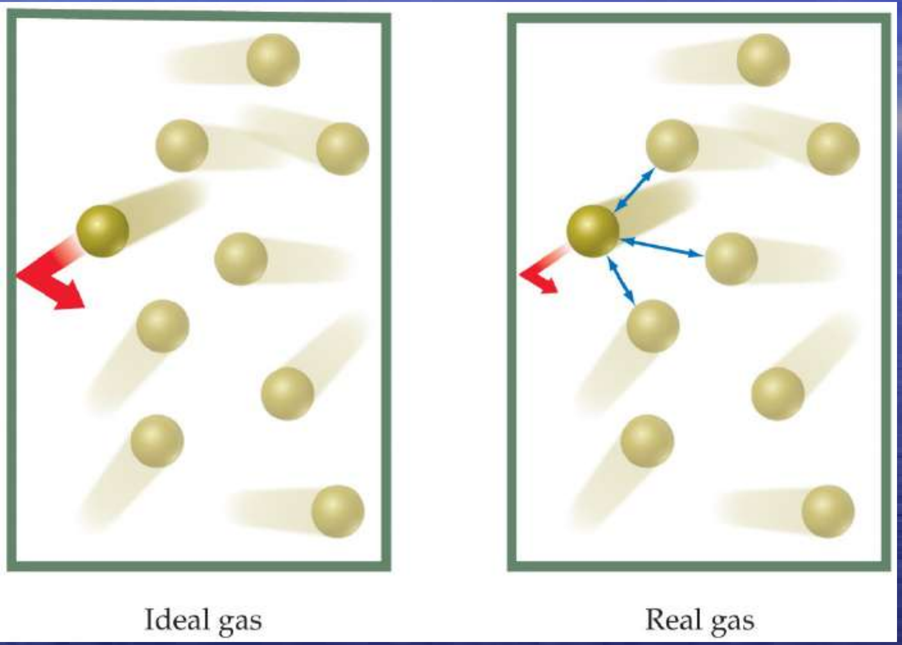


Under which conditions do you expect helium gas to deviate most from ideal behavior?

a. 100 K and 1 atm
b. 100 K and 5 atm
c. 300 K and 2 atm

Deviations from Ideal Behavior





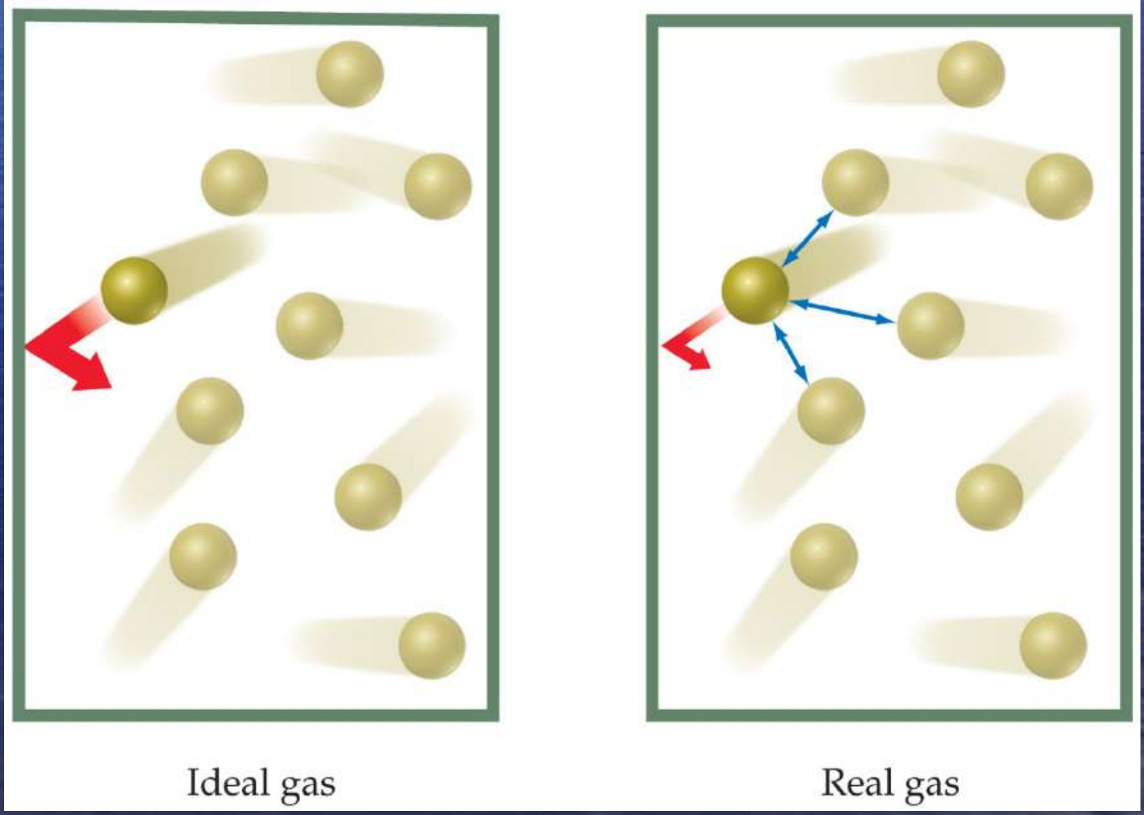
The assumptions made in the kinetic-molecular model (negligible volume of gas molecules themselves, no attractive forces between gas molecules, etc.) break down at high pressure and/or low temperature.

How would you expect the pressure of a gas to change if suddenly the intermolecular forces were repulsive rather than attractive?

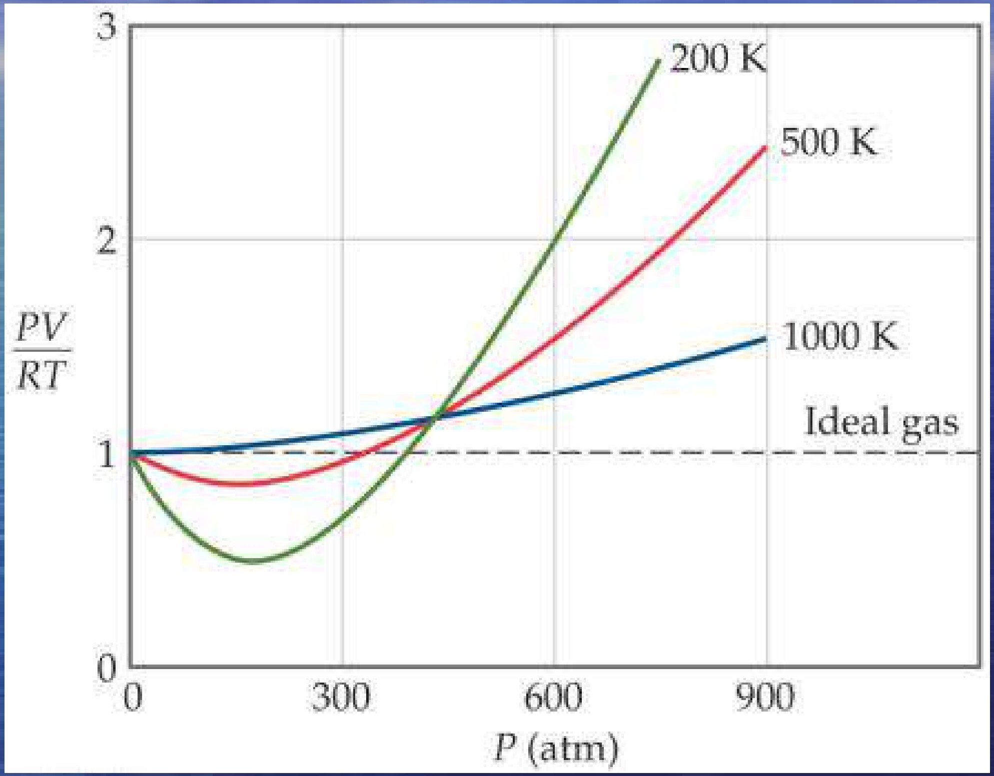
a. Increase

b. Decrease

c.No change



Explain the negative deviation from ideal gas behavior of N_2 below 300 atm.



a. Attractive intermolecular forces

b. Repulsive intermolecular forces

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 pressure adjustment is due to the fact that molecules attract and repel each other.
- The volume adjustment is due to the fact that molecules occupy some space on their own.

The van der Waals Equation

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

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
F_2	1.06	0.0290
Cl_2	6.49	0.0562
H_2O	5.46	0.0305
NH_3	4.17	0.0371
CH_4	2.25	0.0428
CO_2	3.59	0.0427
CCl_4	20.4	0.1383

Integrative Exercise

Cyanogen, a highly toxic gas, is composed of 46.2% C and 53.8% N by mass. At 25ºC and 751 torr, 1.05 g of cyanogen occupies 0.500 L.

- A) What is the molecular formula?
- B) Predict its molecular structure.
- C) Predict the polarity of the compound.