Gas Laws

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Objectives

At the end of this, we will be able to-

- **Know Gas Laws (Boyle, Charles and Ideal Gas Laws);**

- **Explain kinetic molecular theory**
- **Know some applications of Gas Laws.**

Contents

Properties of Gases
Gas Laws-
- **Boyles law**
- **Charles's Law**
- **Combined gas law**
- **Gay-Lussac law, ideal gas law**
- **Dalton's law of partial pressure**
- **Kinetic molecular theory of gas & molecular distribution**
- **Graham's law**

Gas- Properties

- Gas has no definite volume or shape; it fills whatever volume available to it. Gases are highly compressible and expand to occupy the full volume of their containers.

Contrast this to the behavior of a liquid, which always has a distinct upper surface when its volume is less than that of the space it occupies.

- Gases is their low densities, compared with those of liquids and solids.

One mole of liquid water at 298° K and 1 atm pressure occupies a volume of 18.8 cm^3, whereas the same quantity of water vapor at the same temperature and pressure has a volume of 30200 cm^3, more than 1000 times greater.

- They all behave the same way in response to changes in temperature and pressure, expanding or contracting by predictable amounts.

This is very different from the behavior of liquids or solids, in which the properties of each particular substance must be determined individually.

- Gases always form homogeneous mixtures with other gases.

Gas- Pressure

The pressure of a gas is causes by collisions of the molecules with the walls of the container.
The magnitude of the pressure is related to how hard and how often the molecules strike the wall.
The "hardness" of the impact of the molecules with the wall will be related to the velocity of the molecules times the mass of the molecules.
Pressure is the force acting on an object per unit area

$$P = \frac{F}{A}$$
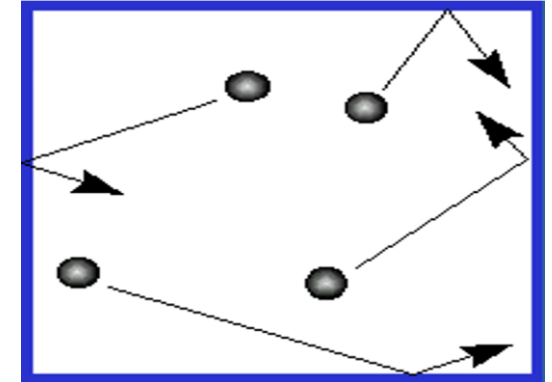
The gravity pulling down on a 1m^2 column of the atmosphere causes a force of 10^5 N. This is air pressure.
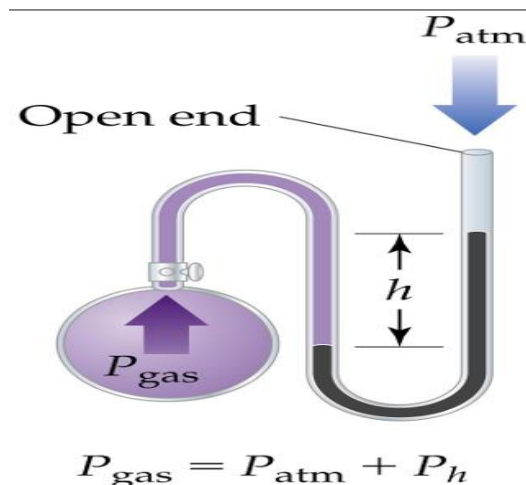SI Units for Pressure: 1 Pascal (Pa) = 1 N/m^2.
Common Standard Pressure Units 1 atm = 760 mmHg = 760 torr = 101.3 kPa

The pressures of gases not open to the atmosphere are measured in manometers.
A manometer consists of a bulb of gas attached to a U-tube containing Hg.

If $P_{gas} < P_{atm}$,
$P_{gas} = P_{atm} - P_h$

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

P_{atm}

Open end

h

P_{gas}

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

Some Common Pressure Units

|		
Atmosphere	atm	
Millimeter of mercury	mmHg	1 atm ≃ 760 mmHg
Torr	Torr	= 760 Torr
Pascal	Pa	= 101,325 Pa
Kilopascal	kPa	= 101.325 kPa
Bar	bar	= 1.01325 bar
Millibar	mbar	= 1013.25 mbar

Absolute Temperature

The absolute temperature is a measure of the average kinetic energy of its molecules.
- If two different gases are at the same temperature, their molecules have the same average kinetic energy.
- If the temperature of a gas is doubled, the average kinetic energy of its molecules is doubled.
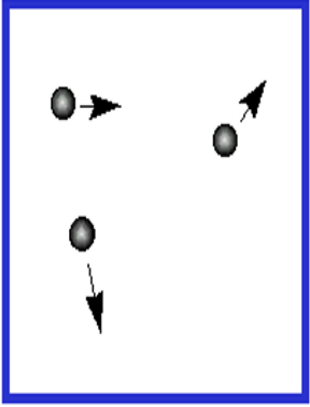
Lower average kinetic energy
Lower absolute temperature
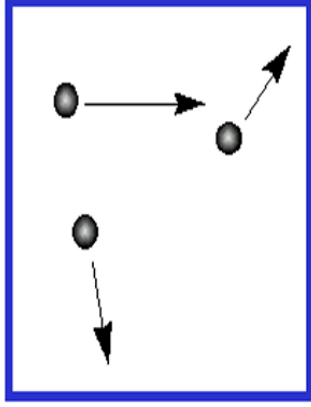
Higher average kinetic energy
Higher absolute temperature

Standard Conditions of Temperature and Pressure

Because gas properties depend on temperature and pressure, it is useful to have a set of standard conditions of temperature and pressure that can be used for comparing different gases. The standard temperature for gases is $0°C = 273.15$ K taken to be and standard pressure, 1 bar = 100 kPa = 10^5 Pa . Standard conditions of temperature and pressure are usually abbreviated as STP.

Standard Temperature and
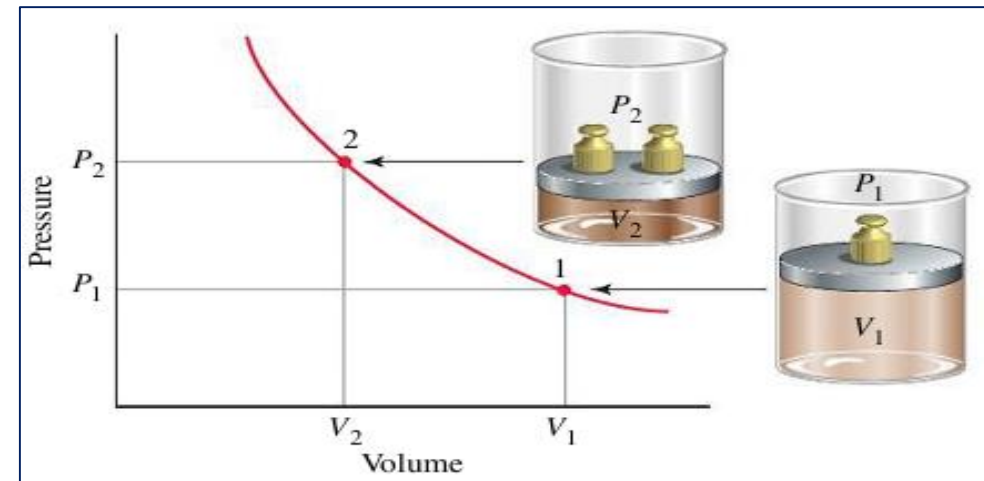Pressure (STP): $0°C$ and 1 bar = 10^5 Pa

Gas Laws- Boyle's Law

This law states that **For a fixed amount of gas at a constant temperature, the gas volume is inversely proportional to the gas pressure.**
Since the temperature is constant (or no heat flow) in this process (Boyle's law), it is referred to as isothermal condition. Mathematically, Boyle's law can be written as:

$$P \propto \frac{1}{V} \quad \text{or} \quad PV = a \,(\text{a constant})$$

When the temperature and amount of gas are held constant, gas volume is inversely proportional to the pressure: A doubling of the pressure causes the volume to decrease to one-half its original value.

Robert Boyle
**Relationship between P and V (T constant)**

When the proportionality sign is replaced with an equal sign and a proportionality constant, the product of the pressure and volume of a fixed amount of gas at a given temperature is seen to be a constant (a). The value of a depends on the amount of gas and the temperature. The graph in Figure is that of PV = a. It is called a hyperbola. The equation, PV = a can be used to derive another equation that is useful for situations in which a gas undergoes a change at constant temperature. If we write the former equation for the initial state (i) and for the final state (f), we get $P_i V_i$ = a, and $P_f V_f$ = a. Because both PV products are equal to the same value of a, we obtain the result,

$$P_i V_i = P_f V_f \quad (n \text{ constant}, T \text{ constant})$$

The equation above is often used to relate pressure and volume changes.

Gas Laws- Charles's Law

The relationship between the volume of a gas and temperature was discovered by the French physicist Jacques Charles in 1787 and, independently, by Joseph Louis Gay-Lussac, who published it in 1802.
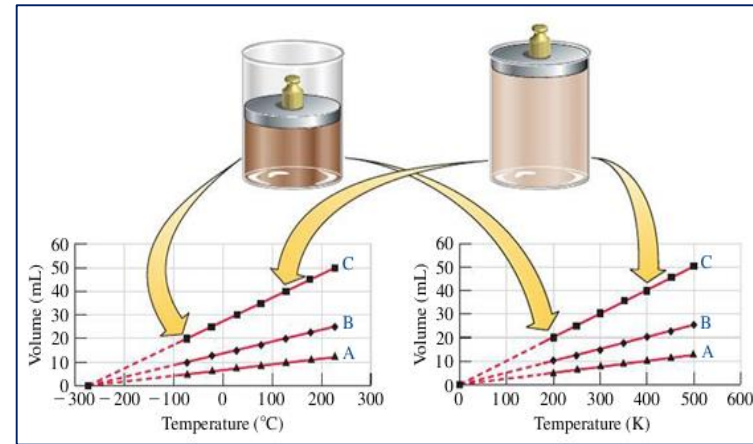
Gas volume as a function of temperature

In Figure, Volume is plotted against temperature on two different scales Celsius and Kelvin. The volumes of three different gases (A, B, and C) are measured at 1 atm and 500 K. As the temperature is lowered, the volume decreases as predicted by Charles's law. Thus, at for example, the volume of gas C has become 25 mL, one-half of the original 50 mL. Although the relationship between volume and temperature is linear for both the Celsius and Kelvin temperature scales, the volume is directly proportional only to the absolute temperature. That is, the volume must be zero at a temperature of zero. Only the Kelvin scale meets this requirement.

The gas volumes all reach a value of zero at the same temperature. The temperature at which the volume of a hypothetical gas becomes zero is the absolute zero of temperature: -273.15 °C on the Celsius scale or 0 K on the absolute, or Kelvin, scale. The relationship between the Kelvin temperature, T, and the Celsius temperature, t, is, $T(K) = t(°C) + 273.15$

This law states that the volume of a fixed amount of gas at constant pressure is directly proportional to the Kelvin (absolute) temperature. In mathematical terms, Charles's law is, $V \propto T$ or $V = bT$ (where b is a constant)
The value of the constant b depends on the amount of gas and the pressure.
It does not depend on the identity of the gas. Doubling the Kelvin temperature of a gas causes its volume to double. Reducing the Kelvin temperature by one-half (say, from 300 to 150 K) causes the volume to decrease to one-half, and so on. An equation that is useful for situations in which a gas undergoes a change at constant pressure. If we apply the equation twice, once for the initial state (i) and once for the final state (f), we get and (V_i/T_i) = b, (V_f/T_f) = b. Because both (V/T) quotients are equal to the same value of b, we obtain the result, $$\frac{V_i}{T_i} = \frac{V_f}{T_f}$$ (n constant, P constant)
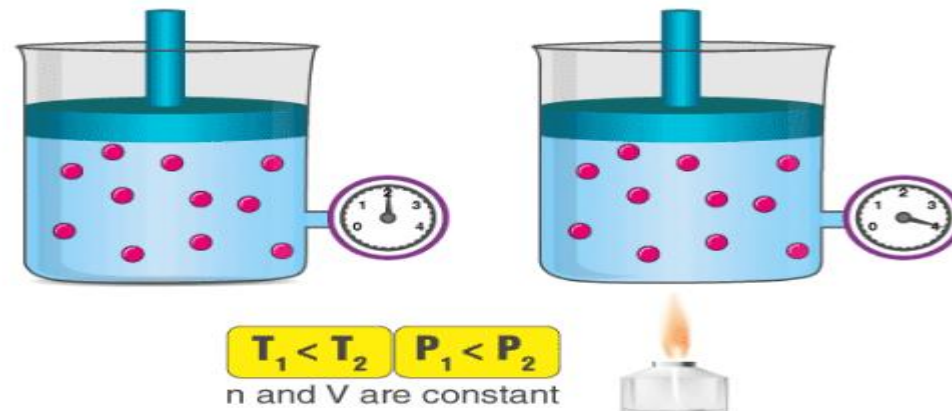
Gay-Lussac's law

Gay-Lussac's law implies that the ratio of the initial pressure and temperature is equal to the ratio of the final pressure and temperature for a gas of a fixed mass kept at a constant volume. This formula can be expressed as follows: $P_1/T_1 = P_2/T_2$; where: P_1 is the initial pressure, T_1 is the initial temperature, P_2 is the final pressure, T_2 is the final temperature

This expression can be derived from the pressure-temperature proportionality for gas. **Since P $\propto$ T for gases of fixed mass kept at constant volume:**

P_1/T_1 = k (initial pressure/ initial temperature = constant), P_2/T_2 = k (final pressure/ final temperature = constant); Therefore, $P_1/T_1 = P_2/T_2$ = k; or, $P_1T_2 = P_2T_1$

Examples of Gay-Lussac's Law

When a pressurized aerosol can (such as a deodorant can or a spray-paint can) is heated, the resulting increase in the pressure exerted by the gases on the container (owing to Gay-Lussac's law) can result in an explosion. This is the reason why many pressurized containers have warning labels stating that the container must be kept away from fire and stored in a cool environment.

$T_1 < T_2$ $P_1 < P_2$
n and V are constant

Avogadro's Law

In 1808, Gay-Lussac reported that gases react by volumes in the ratio of small whole numbers. One proposed explanation was that equal volumes of gases at the same temperature and pressure contain equal numbers of atoms.

In 1811, Amedeo Avogadro resolved this dilemma by proposing not only the equal volumes equal numbers hypothesis, but also that molecules of a gas may break up into half molecules when they react. Using modern terminology, we would say that O_2 molecules split into atoms, which then combine with molecules of H_2 to form H_2O molecules. In this way, the volume of oxygen needed is only one-half that of hydrogen. Avogadro's reasoning is outlined in Figure,

2 vol. H_2 1 vol. O_2 2 vol. H_2O
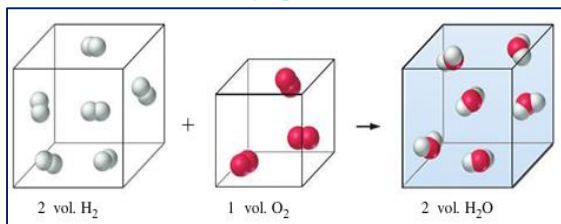
Formation of water actual observation and Avogadro's hypothesis

In the reaction $2\ H_2(g) + 1\ O_2(g) \rightarrow 2\ H_2O(g)$, only one-half as many O_2 molecules are required as are H_2 molecules. If equal volumes of gases contain equal numbers of molecules, this means the volume of $O_2(g)$ is one-half that of $H_2(g)$. The combining ratio by volume is 2:1:2.

Avogadro's equal volumes equal numbers hypothesis can be stated in either of two ways.
- Equal volumes of different gases compared at the same temperature and pressure contain equal numbers of molecules.
- Equal numbers of molecules of different gases compared at the same temperature and pressure occupy equal volumes.

A relationship that follows from Avogadro's hypothesis, often called Avogadro's law, 'At a fixed temperature and pressure, the volume of a gas is directly proportional to the amount of gas'. If the number of moles of gas (n) is doubled, the volume doubles, and so on. A mathematical statement of this fact is,

$$V \propto n \quad \text{and} \quad V = c \times n$$

The constant c, which is equal to V/n, is the volume per mole of gas, a quantity we call the molar volume. Molar volumes of gases vary with temperature and, pressure but experiment reveals that, for given values of T and P, the molar volumes of all gases are approximately equal. The molar volume of a gas is approximately 22.414 L at 0°C and 1 atm and 22.711 L at STP. The following statement summarizes these observations.

$$1\ \text{mol gas} = 22.414\ \text{L}\,(\text{at}\,0\,°C, 1\,\text{atm}) = 22.711\ \text{L}\,(\text{at STP})$$

Combining the Gas Laws: The Ideal Gas Equation and the General Gas Equation

Each of the three simple gas laws describes the effect that changes in one variable have on the gas volume when the other two variables are held constant.

- Boyle's law describes the effect of pressure, $V \propto 1/P$.
- Charles's law describes the effect of temperature, $V \propto T$.
- Avogadro's law describes the effect of the amount of gas, $V \propto n$.

These three laws can be combined into a single equation, the ideal gas equation that includes all four gas variables: volume, pressure, temperature, and amount of gas.

The Ideal Gas Equation

In accord with the three simple gas laws, the volume of a gas is directly proportional to the amount of gas, directly proportional to the Kelvin temperature, and inversely proportional to pressure. A gas whose behavior conforms to the ideal gas equation is called an ideal, or perfect, gas. A value for the constant R, called the gas constant. The value of R depend on which units are used to express pressure and volume. With a molar volume of 22.4140 L and pressure in atmospheres,

$$V \propto \frac{nT}{P} \quad \text{and} \quad V = \frac{RnT}{P}$$

$$PV = nRT$$

$$R = \frac{PV}{nT} = \frac{1 \text{ atm} \times 22.4140 \text{ L}}{1 \text{ mol} \times 273.15 \text{ K}} = 0.082057 \text{ atm L mol}^{-1} \text{ K}^{-1}$$

Using the SI units of m^3 for volume and Pa for pressure gives, $R = \dfrac{PV}{nT} = \dfrac{101{,}325 \text{ Pa} \times 2.24140 \times 10^{-2} \text{ m}^3}{1 \text{ mol} \times 273.15 \text{ K}} = 8.3145 \text{ Pa m}^3 \text{mol}^{-1} \text{K}^{-1}$

The units Pa m^3 M^{-1} K^{-1} also have another significance. The Pascal has units kg m^{-1} s^{-2}, so the units m^3 Pa become kg m^2 s^{-2}, which is the SI unit of energy the joule. Thus R also has the value, $R = 8.3145$ J mol^{-1} K^{-1}. This value of R is used to consider the energy involved in gas expansion and compression.

Common Values of R
$0.082057 \text{ atm L mol}^{-1} \text{K}^{-1}$
$0.083145 \text{ bar L K}^{-1} \text{mol}^{-1}$
$8.3145 \text{ kPa L K}^{-1} \text{mol}^{-1}$
$8.3145 \text{ Pa m}^3 \text{mol}^{-1} \text{K}^{-1}$
$8.3145 \text{ J mol}^{-1} \text{K}^{-1}$

Combining the Gas Laws: The Ideal Gas Equation and the General Gas Equation

What is the volume occupied by 13.7 g Cl_2 (g) at 45 °C and 745 mmHg?

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

$$V = ?$$

$$n = 13.7 \text{ g } Cl_2 \times \frac{1 \text{ mol } Cl_2}{70.91 \text{ g } Cl_2} = 0.193 \text{ mol } Cl_2$$

$$R = 0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1}$$

$$T = 45\,°C + 273 = 318 \text{ K}$$

Divide both sides of the ideal gas equation by P to solve for V.

$$\frac{PV}{P} = \frac{nRT}{P} \qquad \text{and} \qquad V = \frac{nRT}{P}$$

$$V = \frac{nRT}{P} = \frac{0.193 \text{ mol} \times 0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1} \times 318 \text{ K}}{0.980 \text{ atm}} = 5.14 \text{ L}$$

Combining the Gas Laws: The Ideal Gas Equation and the General Gas Equation

What is the pressure in kilopascals, exerted by 1.00×10^{20} molecules of N_2 in a 305 mL flask at 175°C?

$$R = 8.3145 \text{ Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1}$$

$$n = 1.00 \times 10^{20} \text{ molecules N}_2 \times \frac{1 \text{ mol N}_2}{6.022 \times 10^{23} \text{ molecules N}_2}$$

$$= 0.000166 \text{ mol N}_2$$

$$V = 305 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1 \text{ m}^3}{1000 \text{ L}} = 3.05 \times 10^{-4} \text{ m}^3$$

$$T = 175°C + 273 = 448 \text{ K}$$

$$P = \frac{nRT}{V} = \frac{0.000166 \text{ mol} \times 8.3145 \text{ Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1} \times 448 \text{ K}}{3.05 \times 10^{-4} \text{ m}^3}$$

$$= 2.03 \times 10^3 \text{ Pa}$$

$$P = 2.03 \times 10^3 \text{ Pa} \times \frac{1 \text{ kPa}}{1000 \text{ Pa}} = 2.03 \text{ kPa}$$

General Gas Equation (Combined Gas Law)

The ideal gas equation is applied to a single set of conditions (P, V, n, and T). Sometimes a gas is described under two different sets of conditions. Here, the ideal gas equation must be applied twice to an initial condition and a final condition. That is,

Initial condition (i)

$$P_i V_i = n_i R T_i$$

$$R = \frac{P_i V_i}{n_i T_i}$$
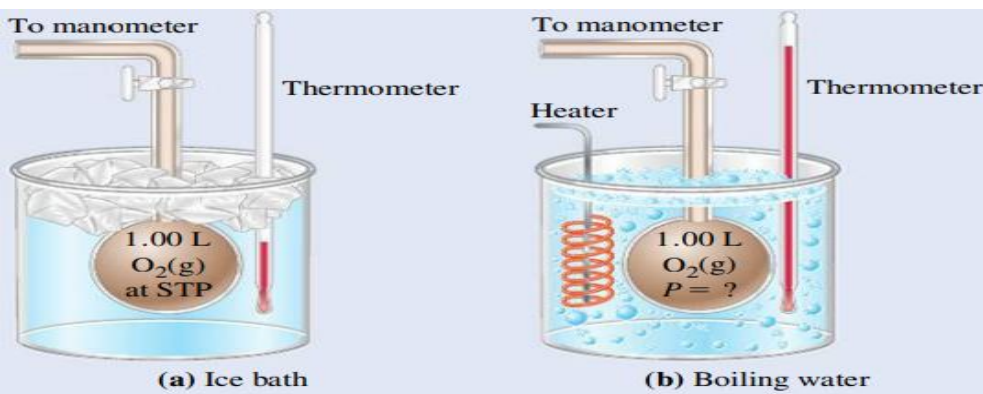
Final condition (f)

$$P_f V_f = n_f R T_f$$

$$R = \frac{P_f V_f}{n_f T_f}$$

$$\frac{P_i V_i}{n_i T_i} = \frac{P_f V_f}{n_f T_f}$$

The above expressions are equal to each other because each is equal to R. This expression is called the general gas equation. It is often applied in cases in which one or two of the gas properties are held constant, and the equation can be simplified by eliminating these constants. For example, if a constant mass of gas is subject to changes in temperature, pressure, and volume, n_i and n_f cancel because they are equal (constant moles); thus we have,

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f} \quad (n \text{ constant})$$

This equation is sometimes referred to as the combined gas law. If both volume and mass are constant, the simple relationship between gas pressure and temperature known as Amontons's law: The pressure of a fixed amount of gas confined to a fixed volume is directly proportional to the Kelvin temperature.

To manometer

Thermometer

1.00 L
$O_2(g)$
at STP

(a) Ice bath

To manometer

Heater

Thermometer

1.00 L
$O_2(g)$
P = ?

(b) Boiling water

In this case, the amount of O_2 is constant ($n_i = n_f$) and the volume is constant ($V_i = V_f$).

$$\frac{P_i V_i}{n_i T_i} = \frac{P_f V_f}{n_f T_f} \quad \text{and} \quad \frac{P_i}{T_i} = \frac{P_f}{T_f} \quad \text{and} \quad P_f = P_i \times \frac{T_f}{T_i}$$

Since $P_i = 1.00$ bar, $T_i = 273$ K, and $T_f = 373$ K, then

$$P_f = 1.00 \text{ bar} \times \frac{373 \text{ K}}{273 \text{ K}} = 1.37 \text{ bar}$$

The situation pictured in Figure (a) is changed to that in Figure (b). What is the gas pressure in Figure (b)? The amount of gas and volume are held constant. (a) 1.00 L $O_2(g)$ at STP; (b) 1.00 L $O_2(g)$ at 100 °C.

Applications of the Ideal Gas Equation- Molar Mass Determination

If we know the volume of a gas at a fixed temperature and pressure, we can solve the ideal gas equation for the amount of the gas in moles (n). Because the number of moles of gas (n) is equal to the mass (m) of gas divided by the molar mass (M), if we know the mass and number of moles of gas, we can solve the expression, n = m/ M for the molar mass, M. An alternative is to make the substitution n = m/ M directly into the ideal gas equation.

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

Suppose, a glass vessel weighs 40.1305 g when clean, dry, and evacuated; it weighs 138.2410 g when filled with water at 25 °C (density of water = 0.9970 g/mL) and 40.2959 g when filled with propylene gas at 740.3 mmHg and at 24 °C What is the molar mass of propylene?

$$\text{mass of water to fill vessel} = 138.2410\ g - 40.1305\ g$$
$$= 98.1105\ g$$

$$\text{volume of water (volume of vessel)} = 98.1105\ g\ H_2O \times \frac{1\ mL\ H_2O}{0.9970\ g\ H_2O}$$
$$= 98.41\ mL = 0.09841\ L$$

$$\text{mass of gas} = 40.2959\ g - 40.1305\ g = 0.1654\ g$$

$$T = 24.0\,°C + 273.15 = 297.2\ K$$
$$P = 740.3\ mmHg \times \frac{1\ atm}{760\ mmHg} = 0.9741\ atm$$

$$M = \frac{mRT}{PV} = \frac{0.1654\ g \times 0.08206\ atm\ L\ mol^{-1}\ K^{-1} \times 297.2\ K}{0.9741\ atm \times 0.09841\ L}$$
$$= 42.08\ g\ mol^{-1}$$

Applications of the Ideal Gas Equation- Gas Densities

To determine the density of a gas, we can start with the density equation, d = m/v. Then we can express the mass of gas as the product of the number of moles of gas and the molar mass: m = n x M This leads to-
With the ideal gas equation, we can replace n/ V by its equivalent, P/ RT to Obtain,

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

$$d = \frac{m}{V} = \frac{n \times M}{V} = \frac{n}{V} \times M$$

The density of a gas at STP can easily be calculated by dividing its molar mass by the molar volume (22.7 L/Mol. For O_2 (g) at STP, for example, the density is 32.0 g/ 22.7 L = 1.41 g/L.

What is the density of oxygen gas (O_2) at 298 K and 0.987 atm?

The molar mass of O_2 is 32 g/mol^{-1},

$$d = \frac{m}{V} = \frac{MP}{RT} = \frac{32.00 \, \text{g mol}^{-1} \times 0.987 \, \text{atm}}{0.08206 \, \text{atm L mol}^{-1} \text{K}^{-1} \times 298 \, \text{K}} = 1.29 \, \text{g/L}$$

Gases in Chemical Reactions

What volume of N_2, measured at 735 mmHg and 26 °C is produced when 75 g of NaN_3 is decomposed?

$$2\,NaN_3(s) \xrightarrow{\Delta} 2\,Na(l) + 3\,N_2(g)$$

$$? \text{ mol } N_2 = 75.0 \text{ g NaN}_3 \times \frac{1 \text{ mol NaN}_3}{65.01 \text{ g NaN}_3} \times \frac{3 \text{ mol } N_2}{2 \text{ mol NaN}_3} = 1.73 \text{ mol } N_2$$

$$P = 735 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.967 \text{ atm}$$

$$V = ?$$

$$n = 1.73 \text{ mol}$$
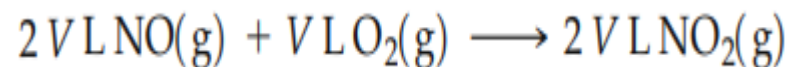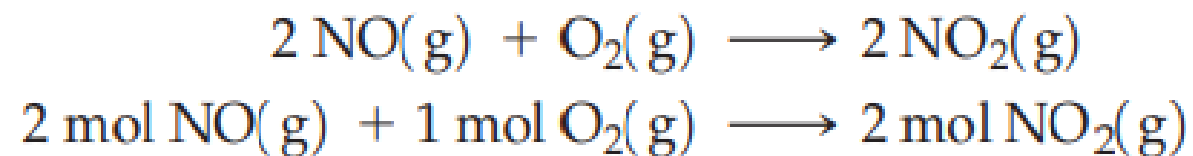
$$R = 0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1}$$

$$T = 26\,°C + 273 = 299 \text{ K}$$

$$V = \frac{nRT}{P} = \frac{1.73 \text{ mol} \times 0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1} \times 299 \text{ K}}{0.967 \text{ atm}} = 43.9 \text{ L}$$

Gases in Chemical Reactions- Law of Combining Volumes

If the reactants and products involved in a stoichiometric calculation are gases, sometimes we can use a particularly simple approach. Consider this reaction.

Suppose the gases are compared at the same T and P. one mole of gas occupies a particular volume, call it V occupy 2V liters; and so on.

$$2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$$

$$2\,mol\,NO(g) + 1\,mol\,O_2(g) \longrightarrow 2\,mol\,NO_2(g)$$

$$2\,V\,L\,NO(g) + V\,L\,O_2(g) \longrightarrow 2\,V\,L\,NO_2(g)$$

If we divide each coefficient by V, we get the following result: $2\,L\,NO(g) + 1\,L\,O_2(g) \longrightarrow 2\,L\,NO_2(g)$

Thus, the volume ratio of the gases consumed and produced in a chemical is the same as the mole ratio, provided the volumes are all measured at the same temperature and pressure. This is Gay-Lussac s law of combining volumes (the volumes of gases involved in a reaction are in the ratio of small whole numbers). The small whole numbers are simply the stoichiometric coefficients in the balanced equation.

Suppose, Zinc blende, ZnS, is the most important zinc ore. Roasting (strong heating) of ZnS in oxygen is the first step in the commercial production of zinc. $2\,ZnS(s) + 3\,O_2(g) \xrightarrow{\Delta} 2\,ZnO(s) + 2\,SO_2(g)$
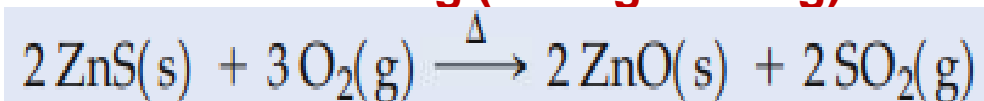
What volume of SO_2 (g)can be obtained from 1 L O_2 (g) and excess ZnS(s)? Both gases are measured at 25 °C and 745 mm Hg.

The stoichiometric factor (shown below in blue) converts from $L\,O_2(g)$ to $L\,SO_2(g)$.

$$?\,L\,SO_2(g) = 1.00\,L\,O_2(g) \times \frac{2\,L\,SO_2(g)}{3\,L\,O_2(g)} = 0.667\,L\,SO_2(g)$$

Mixtures of Gases

Gas laws and the ideal gas equation apply to a mixture of nonreactive gases as well as to individual gases. The simplest approach to working with gaseous mixtures is just to use for the value of n the total number of moles of the gaseous mixture (n_{tot}). As a specific example, consider a mixture of gases in a vessel of fixed volume V at temperature T. The total pressure of the mixture is determined by the total number of moles:

$$P_{tot} = \frac{n_{tot} RT}{V} \qquad (T \text{ constant}, V \text{ constant})$$

For fixed values of T and P, the total volume of a mixture of gases is also determined by the total number of moles:

$$V_{tot} = \frac{n_{tot} RT}{P} \qquad (T \text{ constant}, P \text{ constant})$$

What is the pressure, in bar, exerted by a mixture of 1.0 g H_2 and 5.00 g He when the mixture is confined to a volume of 5.0 L at 20 °C?

$$n_{tot} = \left(1.0 \text{ g } H_2 \times \frac{1 \text{ mol } H_2}{2.02 \text{ g } H_2} \right) + \left(5.00 \text{ g He} \times \frac{1 \text{ mol He}}{4.003 \text{ g He}} \right)$$

$$= 0.50 \text{ mol } H_2 + 1.25 \text{ mol He} = 1.75 \text{ mol gas}$$

$$P = \frac{1.75 \text{ mol} \times 0.0831 \text{ bar L mol}^{-1} \text{ K}^{-1} \times 293 \text{ K}}{5.0 \text{ L}} = 8.5 \text{ bar}$$

Mixtures of Gases- Dalton's Law of Partial Pressure

John Dalton made an important contribution to the study of gaseous mixtures. He proposed that in a mixture, each gas expands to fill the container and exerts the same pressure (called its partial pressure) that it would if it were alone in the container. Dalton s law of partial pressures states that the total pressure of a mixture of gases is the sum of the partial pressures of the components of the mixture, as shown in Figure.

Dalton's law of partial pressures illustrated-
- The pressure of each gas is proportional to the number of moles of gas.
- The total pressure is the sum of the partial pressures of the individual gases.

For a mixture of gases, A, B, and so on,

$$P_{tot} = P_A + P_B + \cdots$$

In a gaseous mixture of n_A moles of A, n_B moles of B, and so on, the volume each gas would individually occupy at a pressure equal to P_{tot} is, $V_A = n_A RT/P_{tot}; V_B = n_B RT/P_{tot}; \cdots$

(a) 5.0 L at 20 °C $P_{H_2} = 2.4$ atm   0.50 mol H_2

(b) 5.0 L at 20 °C $P_{He} = 6.0$ atm   1.25 mol He

(c) 5.0 L at 20 °C $P_{tot} = 8.4$ atm   1.25 mol He / 0.50 mol H_2 / 1.75 mol gas
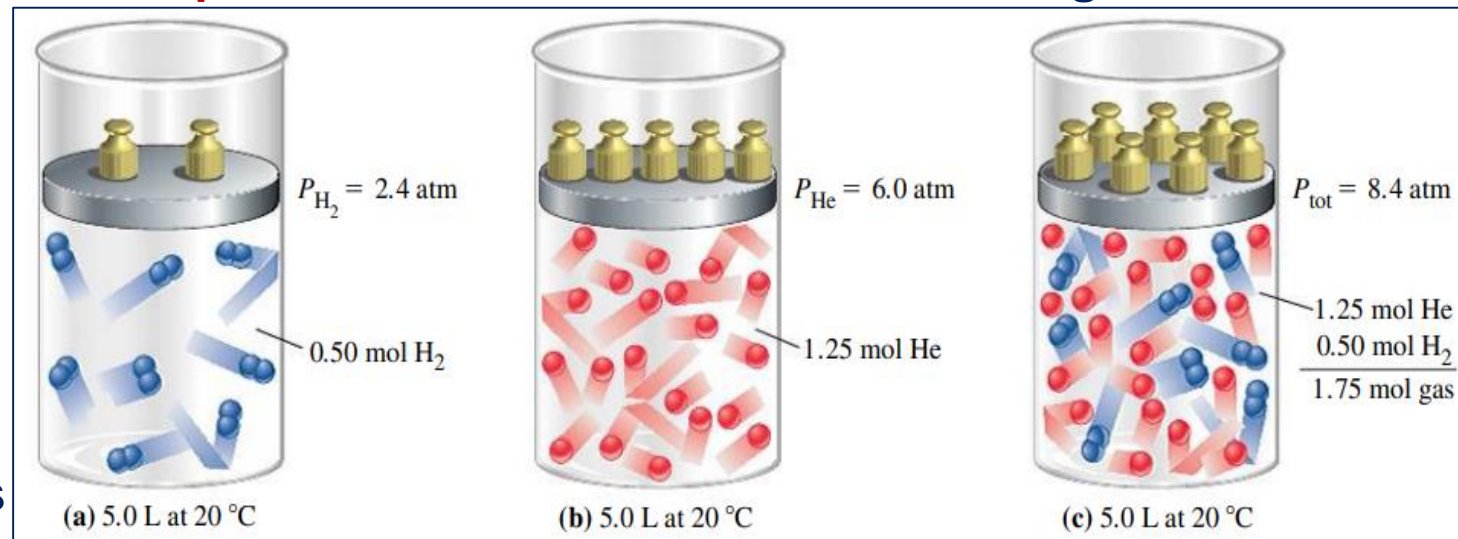
The total volume of the gaseous mixture is, $V_{tot} = V_A + V_B \cdots$
and the commonly used expression percent by volume is,
We can derive an expression from the following ratios,

$$\text{volume} \% \, A = \frac{V_A}{V_{tot}} \times 100\%; \text{Volume} \% \, B = \frac{V_B}{V_{tot}} \times 100\%; \cdots$$

$$\frac{P_A}{P_{tot}} = \frac{n_A(RT/V_{tot})}{n_{tot}(RT/V_{tot})} = \frac{n_A}{n_{tot}} \quad \text{and} \quad \frac{V_A}{V_{tot}} = \frac{n_A(RT/P_{tot})}{n_{tot}(RT/P_{tot})} = \frac{n_A}{n_{tot}}$$

$$\frac{n_A}{n_{tot}} = \frac{P_A}{P_{tot}} = \frac{V_A}{V_{tot}} = x_A$$

The term n_A/n_{tot} is given a special name, the mole fraction of A, X_A. The mole fraction of a component in a mixture is the fraction of all the molecules in the mixture contributed by that component. The sum of all the mole fractions in a mixture is one.

Mixtures of Gases- Dalton's Law of Partial Pressure

What are the partial pressures of and He in the gaseous mixture of 1.0 g H_2 and 5.00 g He when the mixture is confined to a volume of 5.0 L at 20 °C?

One approach involves a direct application of Dalton's law in which we calculate the pressure that each gas would exert if it were alone in the container.

$$P_{H_2} = \frac{n_{H_2} \times RT}{V} = \frac{0.50 \text{ mol} \times 0.0821 \text{ atm L mol}^{-1} \text{K}^{-1} \times 293 \text{ K}}{5.0 \text{ L}} = 2.4 \text{ atm}$$

$$P_{He} = \frac{n_{He} \times RT}{V} = \frac{1.25 \text{ mol} \times 0.0821 \text{ atm L mol}^{-1} \text{K}^{-1} \times 293 \text{ K}}{5.0 \text{ L}} = 6.0 \text{ atm}$$

Expression (6.17) gives us a simpler way to answer the question because we already know the number of moles of each gas and the total pressure from Example 6-11 (P_{tot} = 8.4 atm).

$$P_{H_2} = \frac{n_{H_2}}{n_{tot}} \times P_{tot} = \frac{0.50}{1.75} \times 8.4 \text{ atm} = 2.4 \text{ atm}$$

$$P_{He} = \frac{n_{He}}{n_{tot}} \times P_{tot} = \frac{1.25}{1.75} \times 8.4 \text{ atm} = 6.0 \text{ atm}$$

Kinetic-Molecular Theory of Gases (Assumptions)

- A gas is composed of a very large number of extremely small particles (molecules or, in some cases, atoms) in constant, random, straight-line motion.
- Molecules of a gas are separated by great distances. The gas is mostly empty space. (The molecules are treated as so-called point masses, as though they have mass but no volume.)
- Molecules collide only fleetingly with one another and with the walls of their container, and most of the time molecules are not colliding.
- There are assumed to be no forces between all the others and is unaffected by their presence, except during collisions. molecules except very briefly during collisions. That is, each molecule acts independently of all the others and is unaffected by their presence, except during collisions.
- Individual molecules may gain or lose energy as a result of collisions. In a collection of molecules at constant temperature, however, the total energy remains constant.

Application of the KMT to the Gas Laws-

Effect of a V increase at a constant T

• Constant temperature means that the average kinetic energy of the gas molecules remains constant.

• This means that the speed of the molecules remains unchanged.

• If the speed remains unchanged, but the volume increases, this means that there will be fewer collisions with the container walls over a a given time.

• Therefore, the pressure will decrease (Boyle's Law).

Effect of a T increase at constant V

An increase in temperature means an increase in the average kinetic energy of the gas molecules.

• There will be more collisions per unit time, furthermore, the momentum of each collision increases (molecules strike the wall harder). Therefore, there will be an increase in pressure.

• If we allow the volume to change to maintain constant pressure, the volume will increase with increasing temperature (Charles's Law).


Visualizing molecular motion Molecules of a gas are in constant motion and collide with one another and with the container wall.

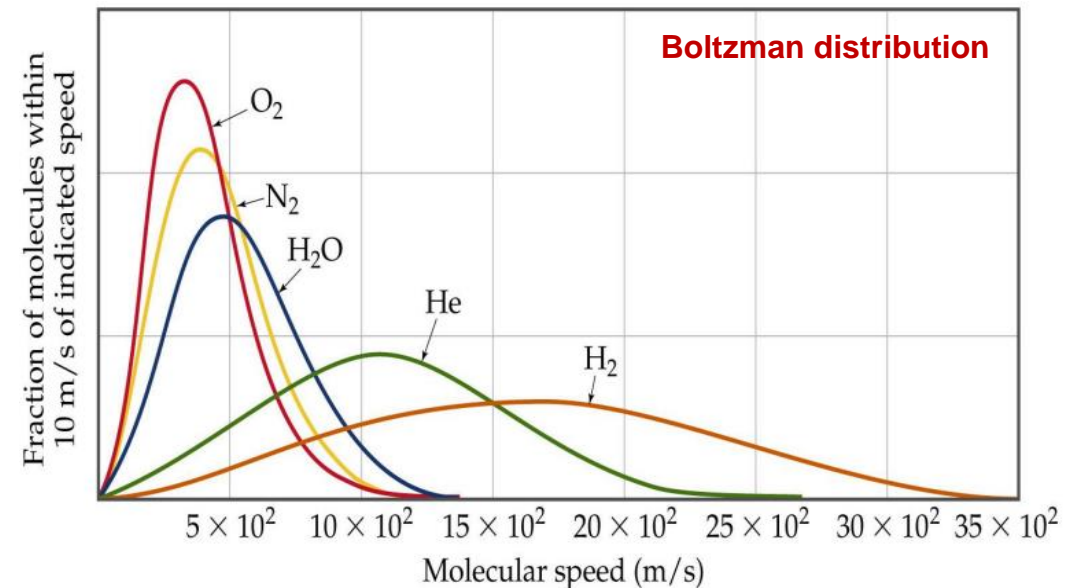# Gas Properties Relating to the Kinetic-Molecular Theory- Distribution of Molecular Speeds

• Not all molecules have the same speed in a sample of gas. When colliding, some particles may speed up and some may slow down, but the total K.E. is constant.
• The higher temperature sample has a higher average speed (as we would expect).
• Higher temps. cause higher kinetic energy because the speed of the molecule increases. (K.E. = 1/2 mv^2)
• Higher temps. will also cause greater pressures in a given volume since there would be more collisions of greater force.
• Larger volumes of gas would have less pressure at a given temp. since there would be less collisions with the walls of the container since the particles would have to travel further before colliding.

Distribution of Molecular Speeds of N$_2$

Conclusions from Boltzman
• Larger gas particles will have a lower average speed.
• Smaller molar masses will travel faster at a given temperature.
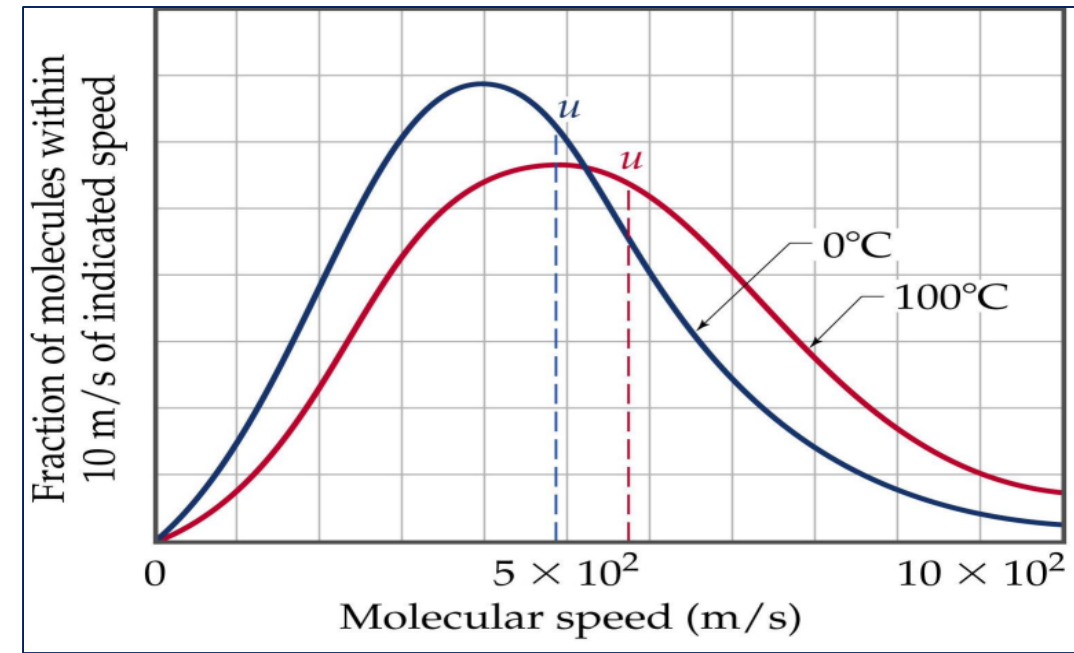
Gas Properties Relating to the Kinetic-Molecular Theory- Graham's Law

Diffusion is the migration of molecules as a result of random molecular motion. The diffusion of two or more gases results in an intermingling of the molecules and, in a closed container, soon produces a homogeneous mixture shown in Figure (a).
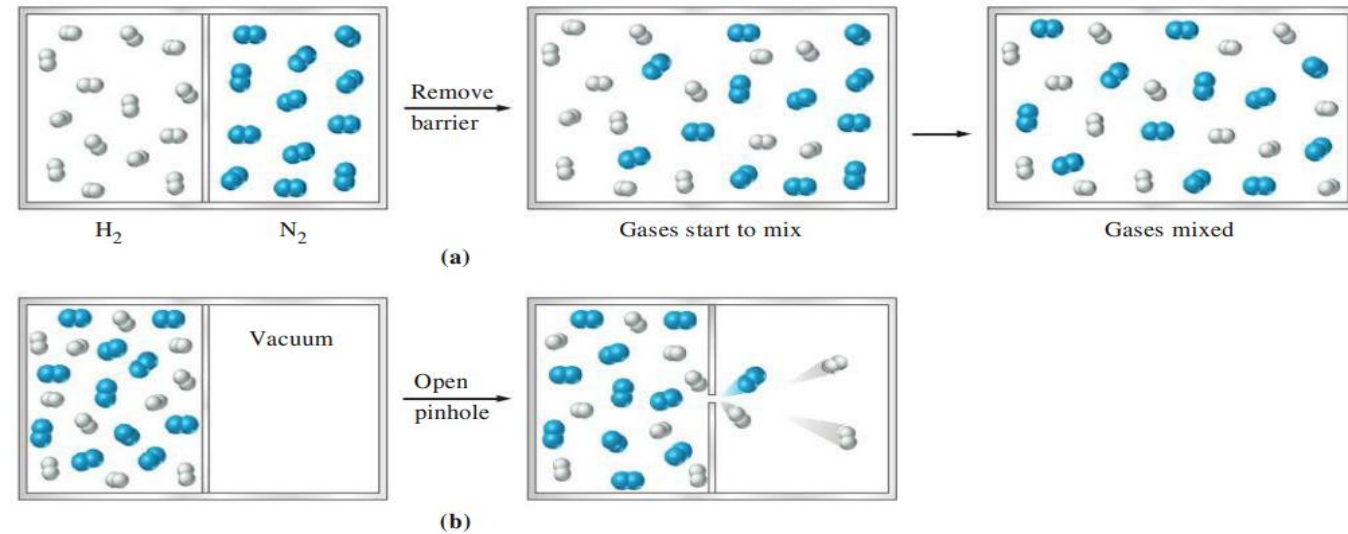
A related phenomenon, effusion, is the escape of gas molecules from their container through a tiny orifice or pinhole. The effusion of a hypothetical mixture of two gases is suggested by Figure (b).

The rate at which effusion occurs is directly proportional to molecular speeds. That is, molecules with high speeds effuse faster than molecules with low speeds. Let us consider the effusion of two different gases at the same temperature and pressure. We can first compare effusion rates with root mean-square speeds and then substitute the expression for these speeds.

(a)

(b)

Diffusion and effusion

a) Diffusion is the passage of one substance through another. In this case, the initially diffuses farther through the because it is lighter, although eventually a complete random mixing occurs.

b) Effusion is the passage of a substance through a pinhole or porous membrane into a vacuum. In this case, the lighter effuses faster across the empty space than does the N_2.

$$u_{rms} = \sqrt{\overline{u^2}} = \sqrt{\frac{3\,RT}{M}}$$

$$\frac{\text{rate of effusion of A}}{\text{rate of effusion of B}} = \frac{(u_{rms})_A}{(u_{rms})_B} = \sqrt{\frac{3\,RT/M_A}{3\,RT/M_B}} = \sqrt{\frac{M_B}{M_A}}$$

The rate of effusion of a gas is inversely proportional to the square root of its molar mass.

Any appropriate units (for example, g/s or mol/min) can be used to express a rate of effusion in equation because in the ratio of two rates, the units cancel. Equation is a kinetic-theory statement of a nineteenth-century law called Graham s law.

Real Gases Vs. Ideal Gases

From the ideal gas equation, we have: PV/RT = n
- For 1 mole of gas, PV/RT = 1 for all pressures & temperatures.
- In a real gas, PV/RT varies from 1 significantly.
- The higher the pressure and colder the temperature, the more the deviation from ideal behavior.
The smaller the distance between gas molecules at higher pressures, the more likely attractive forces will develop between the molecules.
Therefore, the less the gas resembles and ideal gas. (Gases tend to liquefy at higher pressures.)
- As temperature decreases, the gas molecules move slower and closer together so lower temps. mean less energy available to break intermolecular forces.
- Therefore, colder temps. make gases act less ideally. (Gases tend to liquefy at low temperatures).

Gas particles start to take up too much of the volume!
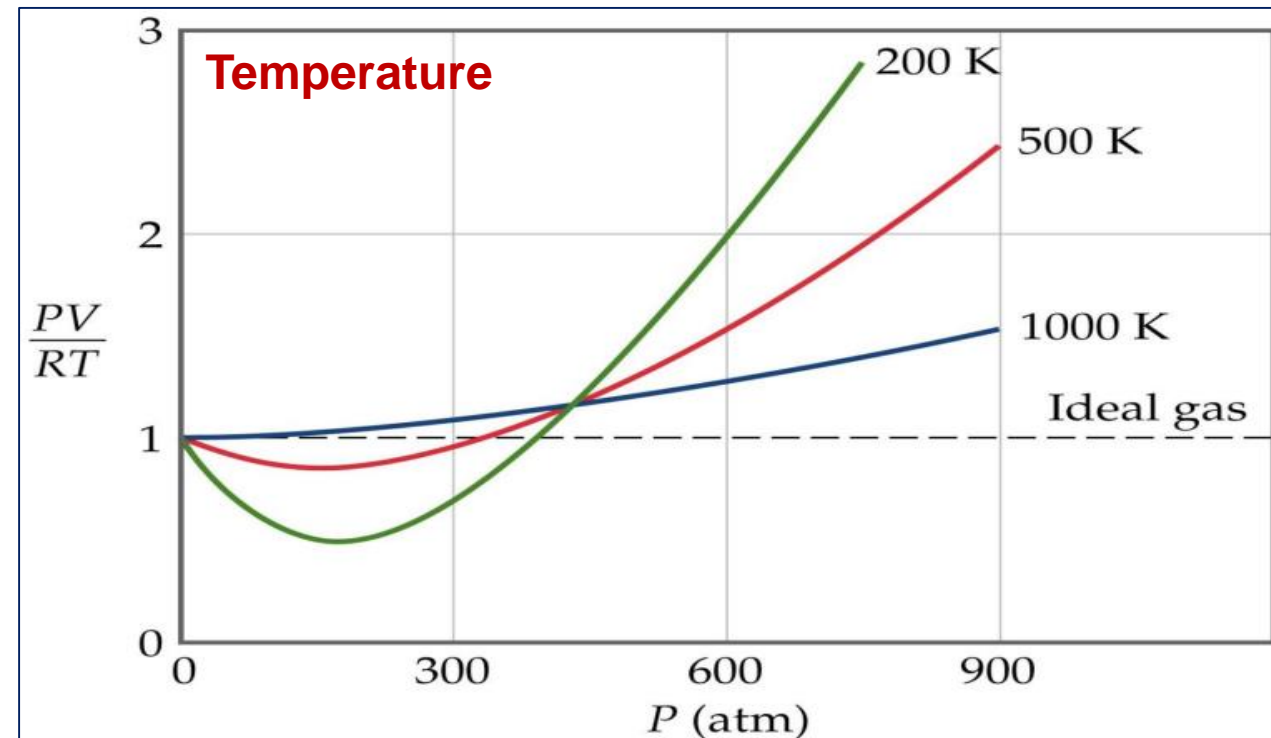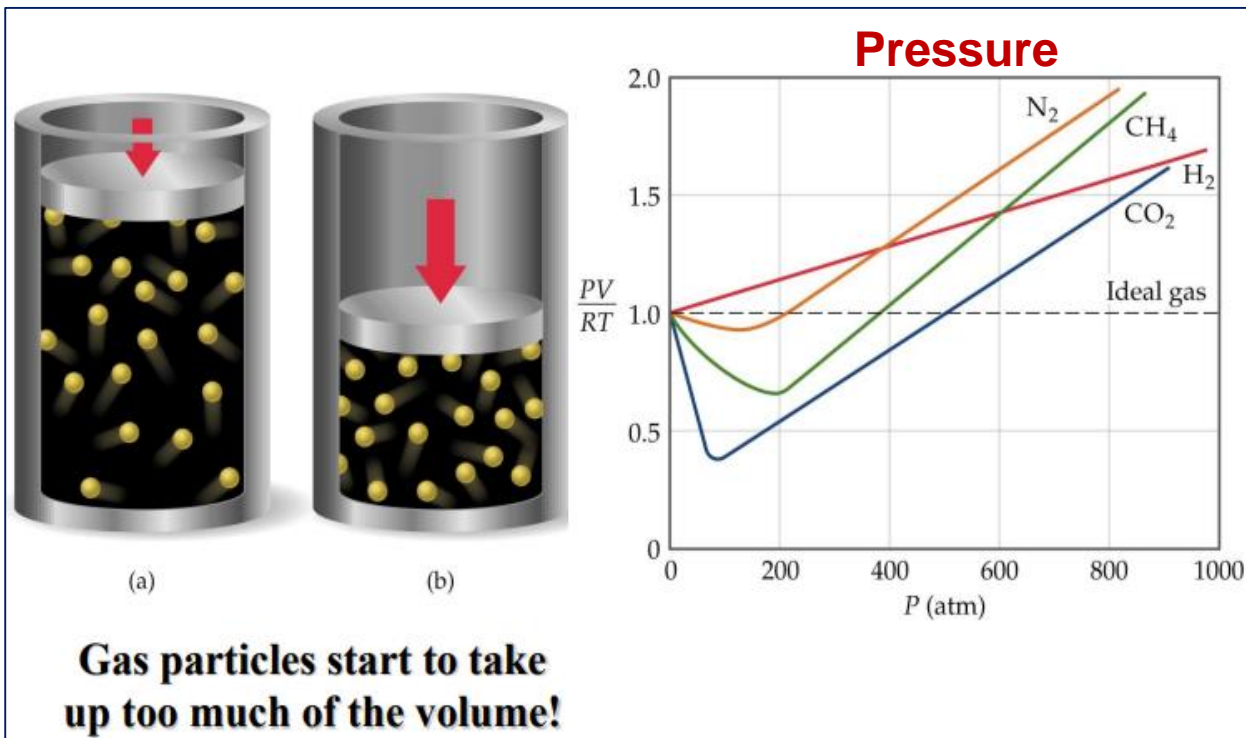
Check List

1. What is the volume occupied by 20.2 g NH_3 (g) at -25 °C and 752 mmHg?
2. At what temperature will a 13.7 g Cl_2 sample exert a pressure of 0.993 bar when confined in a 7.50 L container?
3. How many moles of He(g) are in a 5.00 L storage tank filled with helium at 10.5 atm pressure at 30.0 °C?
4. How many molecules of N_2 (g) remain in an ultrahigh vacuum chamber of 3.45 m³ volume when the pressure is reduced to 6.67 x 10 $^{-7}$ pa at 25 °C?
5. A 1.00 mL sample of N_2 (g) at 36.2 °C and 2.14 atm is heated to 37.8 °C and the pressure changed to 1.02 atm. What volume does the gas occupy at this final temperature and pressure?
6. The glass vessel weighs 40.1305 g is filled with an unknown gas at 772 mmHg and 22.4 °C. The gas-filled vessel weighs 40.4868 g. What is the molar mass of the gas?
7. What is the density of helium gas at 298 K and 0.987 atm? Based on your answer, explain why we can say that 'helium is lighter than air'.
8. The density of a sample of gas is 1.00 g/L at 745 mmHg at 109 °C. What is the molar mass of the gas?
9. How many grams of NaN_3 are needed to produce 20.0 L of N_2 (g) at 30 °C and 776 mmHg?
10. How many grams of Na(l) are produced per liter of N_2 (g) formed in the decomposition of sodium azide if the gas is collected at 25 °C and 1.0 bar?
11. The first step in making nitric acid is to convert ammonia to nitrogen monoxide. This is done under conditions of high temperature and in the presence of a platinum catalyst. What volume of O_2 (g) is consumed per liter of NO(g) formed?

$$4\,NH_3(g) \ + \ 5\,O_2(g) \ \xrightarrow[850\,°C]{Pt} \ 4\,NO(g) \ + \ 6\,H_2O(g)$$
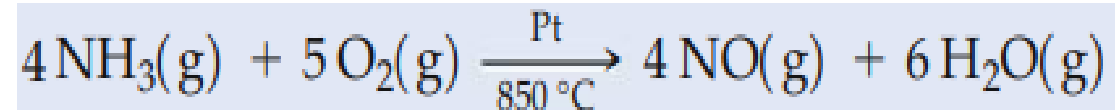
12. If all gases are measured at the same temperature and pressure, what volume of NH_3 (g) is produced when 225 L of H_2 (g) are consumed in the reaction, $N_2(g) \ + \ H_2(g) \ \longrightarrow \ NH_3(g)$ (not balanced)?