



Course Workbook

Discovering Chemical Energetics

2019/2020 EDITION



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Chemistry 1302A/B

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Chapter 1

Gases

Concern for man himself and his fate must always form the chief interest of all technical endeavours...in order that the creations of our minds shall be a blessing and not a curse to mankind. Never forget this in the midst of your diagrams and your equations.

Albert Einstein (1879–1955)

1.1 Gases

OBJECTIVES

After studying this topic, you should be able to:

- Describe the three states of matter at a molecular level.
- Write the mathematical expressions for Boyle's and Charles's law, and apply these laws to problems involving pressure, volume, and temperature.
- Use the ideal gas equation to derive gas pressure, volume, or temperature given the quantities for the remaining terms.

INTRODUCTION

In this topic, the basic properties of gases are discussed and the *ideal gas law*, one of the most important relationships in chemistry, is developed.

Units

The following SI units of measurement will be used in this topic:

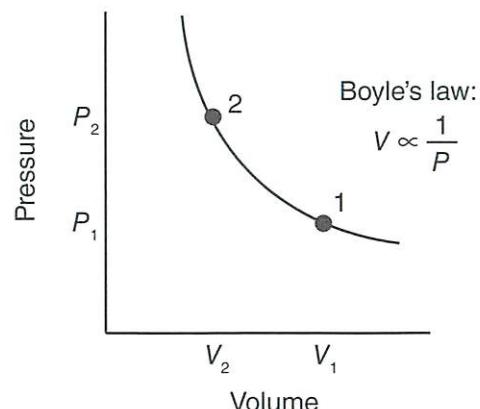
- Pressure = Force per Area = $N\ m^{-2}$ = Pa (pascal)
- 1 bar = 10^5 Pa = 100 kPa
- 1 atmosphere (atm) = 101.33 kPa

THE THREE STATES OF MATTER

The three states of matter studied in chemistry are solid, liquid, and gas.

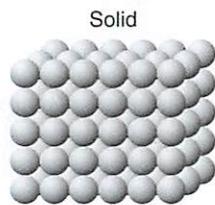
Topics Covered:

- 1.1 Gases
- 1.2 The Ideal Gas Law



Solids

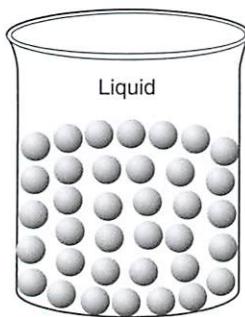
At some temperature, every substance (with the possible exception of helium) will form a solid. In the solid state, atoms, molecules, or ions are locked into a fixed position relative to others in the substance. The forces that hold this “lattice” together can be extremely strong, as is the case with ionic solids, or extremely weak, as is the case with some atomic solids like the inert gases.



The strength of these interactions determines the melting point of the solid in a predictable and obvious way. The stronger the interaction, the higher the melting point. Although atoms or molecules in a solid are not moving relative to each other, they always possess vibrational energy, even at absolute zero, and this vibrational energy increases with temperature. At some point, the magnitude of these vibrational modes overcomes the attractive forces, and the atoms or molecules will lose their fixed positions and become a liquid.

Liquids

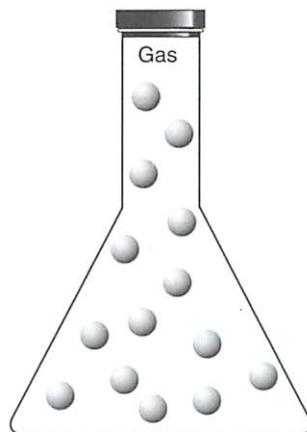
In liquids, the attraction between the atoms or molecules still keeps them touching, although the species are free to move about within a sea of their partners. In the liquid state, a substance will take the shape of the container that holds it.



In the liquid state of a substance, each atom or molecule takes up a little more space than in the solid state due to the increased motion. Therefore, the solid state of a substance is normally denser than its corresponding liquid, and the solid form will sink in its own liquid when the two are at the same temperature. One of the few exceptions to this rule is water. Ice is less dense than water at the same temperature, and, of course, ice floats. This seemingly insignificant observation has profound consequences. If it were not the case, seas, rivers, and lakes would freeze from the bottom up, not the top down, and fish and plant life could not survive in a frozen-solid environment. Indeed, life may not have evolved in the way it has if ice were more dense than water.

Gases

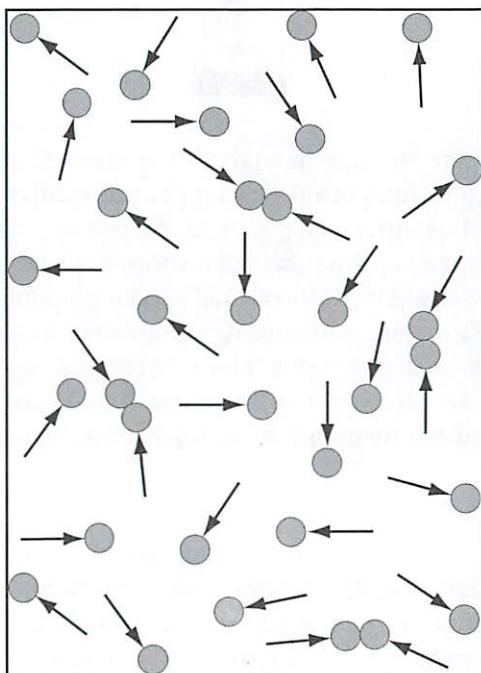
At a high enough temperature, the forces that hold atoms and molecules together are completely overcome, and the atoms or molecules are able to escape from their partner's grip. The substance is now a gas, and each atom or molecule has much more freedom to move around. Atomic motions for typical air gases are in the range of several hundred metres per second, and the gas will expand to fill its container. The collisions of gaseous particles with the walls of the container are the "pressure of the gas" (see image below). The relationship between the amount of gas (in moles), the temperature of the gas, the volume of the container in which it is captured, and the pressure is approximated by the ideal gas law.



THE BEHAVIOUR OF GASES

In the development of chemical laws, theorems, and hypotheses, it is often necessary to make certain approximations and restrictive assumptions under which the theory applies. For the study of gases in this course, it is assumed that:

- the pressure is not too high, and
- the temperature is not close to the condensation temperature.



These assumptions are combined with the following approximations:

1. The atoms or molecules of the gas have no volume. At low pressure, the volume of the atoms or molecules will be very small compared to the total volume of the container, so their volume is indeed negligible.
2. There are no forces acting between the atoms or molecules of the gas. In other words, noncovalent interactions that normally would turn the gas into a liquid are taken to be negligible. This will be the case provided the gas is well above the vapourization/condensation temperature.

Our understanding of the behaviour of gases is based on the work of several scientists.

Boyle's Law

Boyle's law, first published in 1662, is named after Englishman Robert Boyle. Through experimentation, Boyle established the inverse relationship between the pressure of a gas and the volume it occupied, as described by:

$$P \times V = \text{constant}, \text{ or } V \propto \frac{1}{P}$$

where P is the pressure of the gas and V is its volume. In text form, the law reads:

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

As long as the temperature is kept constant and the moles of the gas are fixed, the value of the constant will not change when pressure and volume are varied. Boyle's law is typically used to predict the result of introducing a change, in volume and pressure only, to the initial state of a fixed quantity of gas. So if P_1 and V_1 represent the initial state of the gas, and P_2 and V_2 the final state, then:

$$P_1 V_1 = P_2 V_2$$

Figure 1.1.1 shows the inverse relationship between gas pressure and volume.

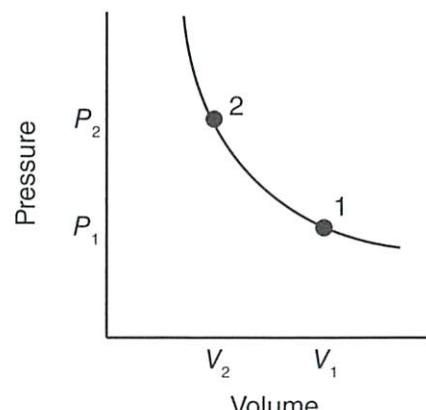


Figure 1.1.1 Inverse relationship between gas pressure and volume.

Example 1.1.1. Applying Boyle's Law

Determine the final volume occupied by an ideal gas when 1.00 L of the gas is compressed from a pressure of 100 kPa to 250 kPa at a constant temperature.

Solution: Since the pressure increases 2.5 times, the volume must decrease by a factor of 2.5. $P_1 = 100 \text{ kPa}$, $P_2 = 250 \text{ kPa}$, $V_1 = 1.00 \text{ L}$. Therefore,

$$V_2 = \frac{100 \text{ kPa} \times 1.00 \text{ L}}{250 \text{ kPa}} = 0.400 \text{ L}$$

Example 1.1.2. Final Pressure after Expansion (In-Class Exercise)

A container fitted with a piston initially at a volume of 1.50 L and a pressure of 125 kPa is allowed to expand at constant temperature to a final volume of 3.50 L. What is the final pressure of the gas inside the container?

Charles's Law

The next important stride in the study of gases came in the early 1800s in France. This was the golden age of hot air ballooning and scientists were anxious to improve the performance of their balloons. Two important French scientists, Jacques Charles and Joseph-Louis Gay-Lussac, made detailed measurements on how the volume of a gas was affected by its temperature.

In the same way that Robert Boyle kept all properties of the gas constant except for the pressure and volume, Jacques Charles kept all properties of the gas constant except for temperature and volume. The volume of the gas increased as the temperature increased, and this was found to be a linear relationship (see Figure 1.1.2). The mathematical expression for Charles's law is:

$$\frac{V}{T} = \text{constant, or } V \propto T$$

In other words, if the temperature (always expressed in K) of a sample of a fixed number of moles of gas is doubled, the volume should double. In text form, Charles's law reads:

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

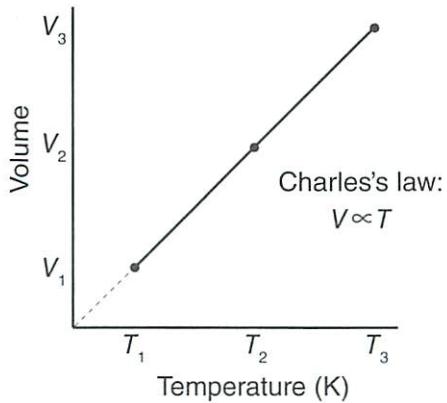


Figure 1.1.2 Linear relationship between gas volume and absolute temperature.

Charles's law can be used to predict the effect of temperature change on the volume of a gas. For a fixed number of moles of gas at a fixed pressure:

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

Charles's law can also be combined with Boyle's law to obtain the following relationship:

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

Thus, for a fixed number of moles of gas:

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

Example 1.1.3. Temperature of a Gas after Heating and Pressure Increase

A gas at 0 °C, 1 bar, is heated at constant volume until $P = 2$ bar. What is the final temperature of the gas?

Solution: Implicit in the question is that n , the amount of gas, is constant. First, convert the temperatures to K and then list the known quantities:

$$P_1 = 1 \text{ bar}; P_2 = 2 \text{ bar}; V_1 = V_2; T_1 = 273.15 \text{ K}; T_2 = ? \text{ K}$$

Next, substitute the known values into:

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

$$\frac{1\text{ bar} \times V_1}{273.15\text{ K}} = \frac{2\text{ bar} \times V_1}{T_2}$$

Therefore: $T_2 = 546.3\text{ K}$.

Example 1.1.4. Pressure of a Gas after Cooling and Compression (In-Class Exercise)

A 15.0 L sample of $\text{N}_2(\text{g})$ at 120.0 kPa and 385 K is compressed to 9.50 L and then cooled to 250 K. What is the final pressure?

Example 1.1.5. Volume of a Gas after Pressure Increase and Heating (In-Class Exercise)

The absolute temperature of a gas inside a balloon doubles while the pressure quadruples. By what factor does the volume of the balloon change?

Avogadro's Law

In 1811, Italian scientist Amedeo Avogadro hypothesized that:

Equal volumes of different gases, at the same temperature and pressure, contain equal numbers of molecules.

This means that if the number of molecules of gas increases, the volume of the gas must also increase in a linear fashion.

Mathematically, this is expressed by:

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

$$\frac{V}{n} = \text{constant, or } V \propto n$$



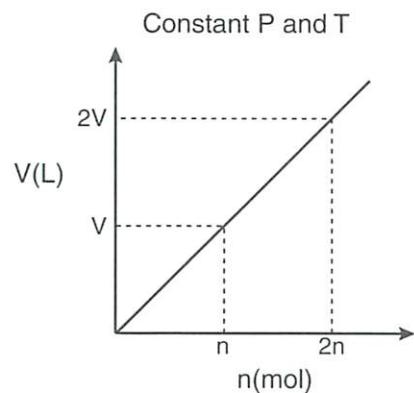


Figure 1.1.3 Linear relationship between gas volume and number of molecules of gas.

Avogadro's law can be used to determine the volume of a gas after the number of molecules (or moles) of gas have changed. The pressure and temperature of the gas must remain constant.

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

Development of the Ideal Gas Law

The "laws" put forward by Boyle, Charles, and Avogadro all relate the volume of gas to some other property of the gas. These three laws may be combined to give one expression that describes "ideal" gas behaviour.

$$\text{Boyle: } V \propto \frac{1}{P}$$

$$\text{Charles: } V \propto T$$

$$\text{Avogadro: } V \propto n$$

Combining the laws, we get: $V \propto \frac{nT}{P}$

This relationship may be converted to an equality by inserting a constant, which is known as R , the ideal gas constant.

$$\text{So, } V = R \times \frac{nT}{P}$$

$$\text{or: } PV = nRT$$

Note that the absolute value of the constant R is the same for all ideal gases but the value used when solving problems depends on the type of problem and the units needed in the solution (see Table 1.1.1).

TABLE 1.1.1 DIFFERENT VALUES OF R USED IN THE IDEAL GAS EQUATION

VALUE	APPLICATION	HOW DERIVED
0.08206 L atm mol ⁻¹ K ⁻¹	V in litres, P in atmospheres	1 atm = 101.33 kPa
0.08314 L bar mol ⁻¹ K ⁻¹	V in litres, P in bar	1 atm = 1.0133 bar
8.314 L kPa mol ⁻¹ K ⁻¹	V in litres, P in kilopascals	1 atm = 101.33 kPa
8.314 J mol ⁻¹ K ⁻¹	Determination of energy (J)	1 L atm = 101.33 J
8.314 kg m ² s ⁻² mol ⁻¹ K ⁻¹	Molecular speed (mass in kg)	1 J = kg m ² s ⁻²
8.314 × 10 ³ g m ² s ⁻² mol ⁻¹ K ⁻¹	Molecular speed (mass in g)	1 J = 10 ³ g m ² s ⁻²

Example 1.1.6. Application of Ideal Gas Equation (In-Class Exercise)

15.0 g of sulfur dioxide, SO₂(g), occupy a volume of 4.00 L at 105 °C. What is the pressure of the gas in kPa?

Section 1.1 Practice Problems

1. A sample of air in a balloon initially at a volume of 2.00 L and a pressure of 100 kPa is allowed to expand at a constant temperature to 3.00 L. What is the final pressure inside the balloon?
2. A 1.00 L sample of $\text{CO}_2(\text{g})$ at 200 K is heated to 400 K and allowed to expand at a constant pressure. What is the final volume?
3. A sample of butane (C_4H_{10}) at 100 kPa and 298 K is heated to 398 K at a constant volume. What is the pressure after heating?
4. If equal masses of the gases Xe, Ar, and Ne are placed in separate flasks of equal volume at the same temperature, which one of the following statements is correct?
 - a. The pressure in the Ne flask is the greatest.
 - b. The pressure in the Ar flask is the greatest.
 - c. The pressure in the Xe flask is the greatest.
 - d. All flasks contain the same number of atoms.
 - e. The pressure in all of the three flasks is the same.
5. If equal masses of O_2 and N_2 are placed in identical containers at the same temperature, which one of the following statements is correct?
 - a. Both containers contain the same number of molecules.
 - b. There will be more molecules in the O_2 flask than the N_2 flask.
 - c. The pressure in the N_2 flask will be greater than the pressure in the O_2 flask.
 - d. None of the other statements is correct.
 - e. This question can't be answered unless the masses of O_2 and N_2 in the flasks are known.
6. A 20.0 L sample of air at 104.0 kPa and 400 K is cooled to 300 K and the volume of the container is reduced to 15.0 L. What is the final pressure of the system?

7. The air inside a rubber balloon at 80 °C has a pressure of 140 kPa. After cooling, the balloon's volume is reduced by 10%, and its inside pressure decreases to 125 kPa. What is the final temperature, in °C, inside the cooled balloon?
8. The density of liquid water at its boiling point of 100.0 °C is 0.96 g mL⁻¹. Calculate the factor by which liquid water at 100.0 °C expands (i.e., the ratio $V_{\text{steam}}/V_{\text{liquid}}$) when it turns into steam at 100.0 °C and 101 kPa pressure. Hint: Think of what happens to *one mole* of water on evaporation.
9. What pressure would 10.0 g of molecular nitrogen, N₂, exert at 120.0 °C if it occupies a volume of 2.50 L?
10. 8.80 g of CO₂(g) occupies a volume of 12.0 L at 54.5 kPa pressure. What is its temperature?
11. Xenon (Xe) filled lamps are used in the automobile industry. What mass, in g, of Xe gas is contained in a 65.0 mL lightbulb at 553 kPa pressure at 25 °C?
12. If 100 g of sulfur is burned to produce SO₂(g), what pressure (in kPa) would the product exert in a volume of 200 L at 40.0 °C?
13. Commercially, nitrogen is sold as a compressed gas contained in cylinders. If a cylinder of volume 116 L is filled with N₂ to a pressure of 1.38×10^4 kPa at 25.0 °C, what mass of N₂ does the cylinder contain? Assume ideal gas behaviour.
14. Regarding the above, if the tap were opened and the gas allowed to escape, how many litres of N₂ gas at 100 kPa pressure and 25.0 °C would come out of the cylinder?
15. A 10.0 L container is initially filled with propane (C₃H₈) at a pressure of 50.0 kPa and a temperature of 28.0 °C. One mole of Ar gas is then added and the mixture is heated to 90.0 °C. What is the final pressure, in kPa, in the container?
16. An evacuated 560 mL light bulb was found to weigh 14.56 g. When filled with the vapour of a volatile compound at 100.0 °C and 98.7 kPa, the bulb weighed 17.09 g. Analysis of the compound showed it to contain 84.4% carbon and 15.6% hydrogen by mass. Determine the molar mass and the molecular formula of the compound.

17. Which of the following statements is/are correct for two moles of an ideal gas?

- a. A plot of P versus T at constant V will give a straight line.
- b. A plot of V versus T at constant P will give a straight line with slope = R/P .
- c. A plot of PV/T versus P will give a straight line with a zero slope.
- d. A plot of PV versus T will give a straight line with a zero slope.
- e. A plot of PV/RT versus P will give a straight line with a slope = 2.

1.2 The Ideal Gas Law

OBJECTIVES

After studying this topic, you should be able to:

- Use the ideal gas law to determine densities and molar masses.
- Describe and apply Dalton's law and the relationship between partial pressure and mole fraction.
- Perform stoichiometric calculations using gas volumes and/or pressures.
- Describe and apply Graham's law and the relationship between molecular mass, effusion rate, and enhancement factor.

INTRODUCTION

In the previous topic, Boyle's law, Charles's law, and Avogadro's law were reviewed, and their contribution to the development of the ideal gas law ($PV = nRT$) was explained. In this topic, the ideal gas law is discussed in detail, and more complex scenarios are presented. The kinetic theory of gases is also introduced.

THE MOLAR VOLUME OF A GAS

For solids and liquids, the mass and volume of one mole of a substance depends on the substance being considered. For example, one mole of sulfuric acid (H_2SO_4) weighs 98 g and occupies 54 mL, while one mole of benzene (C_6H_6) weighs 78 g and occupies 89 mL.

Although different gases have different molar masses, Avogadro's law states that one mole of any ideal gas always occupies the same volume at a given temperature and pressure, regardless of the gas in question. This also means that equal volumes of different gases at the same temperature and pressure contain the same number of moles.

According to the ideal gas law, the volume of one mole of an ideal gas at 0 °C and 1 atm is:

$$V = \frac{nRT}{P} = \frac{(1 \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(273.15 \text{ K})}{(1 \text{ atm})} = 22.4 \text{ L}$$

0 °C (273.15 K) and 1 atm (101.33 kPa) are called *normal temperature and pressure* (NTP), and are common reference conditions used when defining the properties of gases. The volume 22.4 L is known as the *normal volume of an ideal gas* at NTP. Previously, these conditions were usually called *standard temperature and pressure*, which is the name still used in many texts.

VARIATIONS OF THE IDEAL GAS LAW

The ideal gas law can be used to determine the molar mass of a gas at fixed volume, temperature, and pressure. The density (d) of any substance is defined as the mass occupied per unit volume:

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

In turn, the mass of any substance is related to its molar mass (MM) and the number of moles (n):

$$m = MM \times n$$

The ideal gas equation, $PV = nRT$, can then be used to derive a general relationship between gas density and its molar mass:

$$d = \frac{(MM)P}{RT} \text{ or } MM = \frac{dRT}{P} \quad (1.2.1)$$

Equation 1.2.1 shows that, at constant temperature, gas density is directly proportional to its pressure. In addition, at constant pressure and temperature, density is related to the molar mass of a gas.



Example 1.2.1. Density and Molar Mass of a Gas

A 5.00 L flask holds 18.55 g of a gas at 115 °C and 1.00 atm. What is (a) the density of the gas under these conditions, and (b) its molar mass?

Solution:

a. $d = \frac{m}{V} = \frac{18.55\text{ g}}{5.00\text{ L}} = 3.71\text{ g L}^{-1}$

b. Equation 1.2.1 can be used to find the molar mass: $MM = \frac{dRT}{P}$

$R = 0.08206\text{ L atm mol}^{-1}\text{ K}^{-1}$ when V is in L and P is in atm. Convert the temperature from °C to K. Then:

$$MM = \frac{(3.71\text{ g L}^{-1})(0.08206\text{ L atm mol}^{-1}\text{ K}^{-1})(388.15\text{ K})}{(1.00\text{ atm})} = 118.23\text{ g mol}^{-1}$$

Example 1.2.2. Molar Mass and Molecular Formula of a Gas (In-Class Exercise)

A gas with the formula SO_x has a density of 2.968 g L⁻¹ at 35 °C and 95.0 kPa.

Determine the following:

- The molar mass of the gas.
- The value of x .

DALTON'S LAW OF PARTIAL PRESSURES

In the case of a mixture of several ideal gases, the total volume of the mixture, the total pressure, and total number of moles behave as a single gas with respect to the ideal gas law:

$$PV = nRT \text{ or } P_{\text{total}} \times V_{\text{total}} = n_{\text{total}} \times R \times T$$

Each of the constituents in a gas mixture is said to exhibit a *partial pressure* that contributes to the total pressure. The relationship between the partial pressures and total pressure of a gas mixture was first proposed by Englishman John Dalton in 1801. Dalton's law of partial pressures states:

The total pressure exerted by a mixture of gases is the sum of all the partial pressures of these gases.

Dalton's law is illustrated in Figure 1.2.1 for three gases. For a mixture of three gases (A, B, and C), the total pressure would be:

$$P_T = P_A + P_B + P_C$$

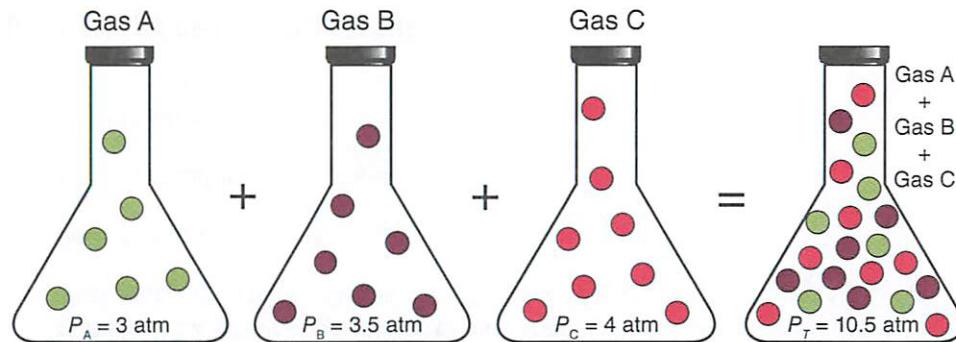


Figure 1.2.1 Dalton's law of partial pressures.

Mole Fractions and Partial Pressure

If n_i is the number of moles of an individual constituent in a gas mixture and n_T is the total number of moles in the mixture, the *mole fraction*, X_i , is:

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

At a constant temperature and volume, the pressure is directly proportional to the moles. This means:

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

which can be arranged to give: $P_i = X_i P_T$

Dalton's Law says that the sum of the partial pressures, P_A , P_B , and P_C of a mixture of ideal gases A, B, and C equals the total pressure, P_T . If the pressures of each gas are expressed in terms of the mole fractions, then: $P_A = X_A P_T$, $P_B = X_B P_T$, and $P_C = X_C P_T$. Note that the sum of all the mole fractions is always 1. In other words, $X_A + X_B + X_C = 1$.



The ideal gas law can be applied to each individual constituent of a gas mixture, as well as the gas mixture as a whole. For each constituent, the ideal gas law can be written as:

$$P_i V = n_i RT$$

Example 1.2.3. Partial Pressure and Mole Fraction of a Gas (In-Class Exercise)

Flask A and Flask B are connected by a stopcock. Flask A has a volume of 400 mL and initially contains $O_2(g)$ at a pressure of 90.0 kPa. Flask B has a volume of 700 mL and initially contains $N_2(g)$ at a pressure of 70.0 kPa. The stopcock is opened and the gases mix. The temperature is held constant.

Determine the following:

- a. The partial pressure of each gas after mixing.
- b. The total pressure.
- c. The mole fraction of each gas in the final mixture.

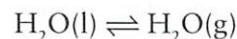
From Avogadro's law, we know that at constant temperature and pressure, the volume of a gas is directly proportional to the number of moles.

Example 1.2.4. Partial Pressures of Atmospheric Gases (In-Class Exercise)

By volume, air contains 78% nitrogen (N_2), 21% oxygen (O_2), and the remaining 1% is composed of rare gases (argon), carbon dioxide, and variable amounts of water vapour, etc. Determine the partial pressure of each of the two main constituents (N_2 and O_2) at an altitude where the atmospheric pressure is 0.80 atm.

Vapour–Liquid Equilibrium and Vapour Pressure

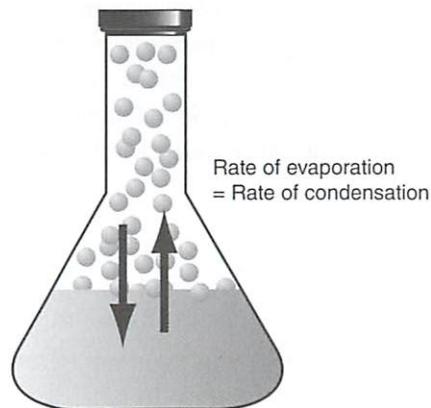
Suppose a flask was partially filled with water and, before being stoppered, the air in the flask was replaced with nitrogen gas. Some of the liquid water will evaporate until an equilibrium state is reached. At equilibrium, the rates of evaporation and condensation will be the same, and the pressure of the $\text{H}_2\text{O}(g)$ will remain constant.



At this point, the total pressure of the gas in the flask would be equal to the N_2 pressure plus the pressure added by the gaseous H_2O molecules:

$$P_{\text{total}} = P_{\text{nitrogen}} + P_{\text{water}}$$

The partial pressure of the water vapour (P_{water}) is referred to as the *vapour pressure* of water. The vapour pressure of water depends *only* on the temperature of water; it does not depend on the volume of the container or the presence of another gas. At higher temperatures, vapour pressure increases as more energy is provided to the liquid molecules, allowing them to escape into the gas phase. Solvents that are more volatile (i.e., have lower boiling points) have higher vapour pressures. The boiling point is defined as the temperature at which the vapour pressure of a liquid is equal to atmospheric pressure.



Example 1.2.5. Vapour Pressure and the Mass of a Gas Collected over Water (In-Class Exercise)

A sample of O₂ gas collected at 37 °C over water with the same temperature has a volume of 15.0 L and a total pressure of 102.0 kPa. What is the mass, in grams, of the O₂ in the sample? The vapour pressure of water at 37 °C is 6.3 kPa.

Average Molar Mass of a Mixture

The average molar mass, \overline{MM} , of a mixture of different gases (e.g., gas A, gas B, gas C, etc.) is the weighted average of the molar masses of the different components. Mathematically, this can be represented as:

$$\overline{MM} = (X_A \times MM_A) + (X_B \times MM_B) + (X_C \times MM_C)$$

Since \overline{MM} is based on a weighted average, its value is usually closest to the molar mass of the component in the greater quantity.

Example 1.2.6. Average Molar Mass of a Mixture of Gases (In-Class Exercise)

A sample contains 0.123 moles O₂(g), 0.568 moles N₂(g), and 1.68 moles Cl₂(g). What is the average molar mass of this mixture?

Example 1.2.7. Average Molar Mass and Density of a Mixture of Gases (In-Class Exercise)

A gaseous mixture of ethane, C₂H₆(g), and propane, C₃H₈(g), exerts a total pressure of 85.0 kPa at 20 °C. If the pressure of ethane is 40.0 kPa, what is the density of the mixture?

GAS REACTION STOICHIOMETRY

The ideal gas law, $PV = nRT$, shows that at constant temperature and pressure, the volume of a gas is directly proportional to the number of moles. Likewise, at constant temperature and volume, the pressure of a gas is directly proportional to the number of moles. Therefore, in the stoichiometry of gas reactions, the stoichiometric coefficients of gaseous reactants and products (i.e., the number of moles) are directly related to the volume and pressure. When the pressure and temperature are constant, mole ratios are the same as volume ratios. Likewise, at constant volume and temperature, mole ratios are the same as pressure ratios.

The typical gas stoichiometry scenarios encountered in chemistry are:

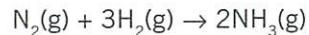
1. Mole–volume
2. Mass–volume
3. Volume–volume
4. Pressure–pressure

The meaning of these scenarios will become clear in the following examples.

Example 1.2.8. Stoichiometric Relationship between Moles and Volume

In the Haber-Bosch process, hydrogen gas and nitrogen gas react over an iron substrate to produce ammonia, which is used in the production of fertilizer. Given this process, how many litres of NH_3 can be produced at $27.0\text{ }^\circ\text{C}$ and 1.0 atm if 20.0 moles of N_2 are reacted with excess hydrogen?

Solution: Start with the balanced equation:



According to the balanced equation, 1 mole of N_2 and 3 moles of H_2 will give 2 moles of NH_3 . Similarly, if 20 moles of N_2 are consumed, 40 moles of NH_3 can be produced. Use the ideal gas law to find the volume of NH_3 .

$$V = \frac{nRT}{P} = \frac{(40.0\text{ mol})(0.08206\text{ L atm mol}^{-1}\text{ K}^{-1})(300.15\text{ K})}{(1.0\text{ atm})} = 990\text{ L}$$

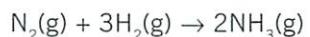


Example 1.2.9. Stoichiometric Relationship between Mass and Volume

In this example, the mass of one component is known and the volume of another component must be determined at a stated temperature and pressure.

Referring again to the Haber-Bosch process, how many litres of H₂ will be required at a temperature of 300.15 K and 3.0 atm pressure to consume 56.0 grams of N₂?

Solution:

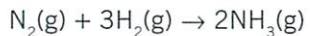


56.0 grams of N₂ corresponds to 2.00 moles of N₂ ($MM = 28.0 \text{ g mol}^{-1}$). To consume 2 moles of N₂, 6.00 moles of H₂ are needed. Using the given temperature and pressure, find the volume occupied by 6.00 moles of H₂:

$$V = \frac{nRT}{P} = \frac{(6.00 \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(300.15 \text{ K})}{(3.0 \text{ atm})} = 50 \text{ L}$$

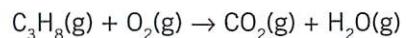
Example 1.2.10. Stoichiometric Relationship Based on Volume Change (In-Class Exercise)

Referring again to the Haber-Bosch process, how many litres of NH₃ can be produced if 10 litres of N₂ are consumed? The volumes are measured at the same temperature and pressure.



Example 1.2.11. Stoichiometric Relationship Based on Pressure Change (In-Class Exercise)

A sealed vessel contains propane gas and oxygen gas with partial pressures of 60 kPa and 200 kPa, respectively. The mixture is reacted according to the following unbalanced equation:



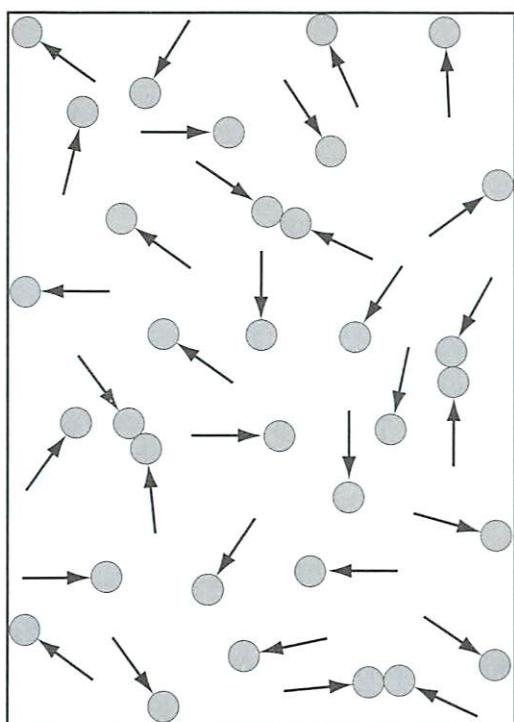
and then cooled to the initial temperature.

- a. What is the partial pressure of the CO_2 produced?
 - b. What is the partial pressure of the excess reagent after the reaction?
 - c. What is the total pressure of the gaseous mixture?
 - d. What is the mole fraction of H_2O in the gaseous mixture?
-



THE KINETIC MOLECULAR THEORY OF GASES

The ideal gas law describes the observable behaviour of gases, but does not provide any insight into what happens to a gas at the molecular level, and does not explain how the behaviour of gas molecules results in the relationships embedded in $PV = nRT$.



In the 19th century, detailed analysis of gaseous atoms and molecules by physicists Rudolf Clausius, James Clerk Maxwell, and Ludwig Boltzmann led to the development of the *kinetic molecular theory* of gases. The kinetic molecular theory of gases is based on the following assumptions:

1. The size of molecules is negligible when compared to the space between them and the volume of their container.
2. Molecules moving through space are considered to be *point particles*. As such, they do not have any vibrational or rotational energy, just translational (kinetic) energy.

3. The collisions that occur between molecules, and between molecules and their container, are considered elastic. That is, the total momentum and energy of colliding molecules are conserved during the collisions, and the molecules move in straight lines at constant velocities. Moreover, gas pressure is the result of molecules colliding with the container walls (see image on previous page).
4. There are no attractive or repulsive forces between the molecules.
5. The average kinetic energy of the molecules is proportional to the temperature (T) in Kelvin. When the temperature is increased, the kinetic energy increases. The kinetic energy of the gas molecules is given by:

$$\overline{E_K} = \frac{1}{2}m\bar{u}^2 \quad (1.2.2)$$

where m is the mass of one molecule and u is the speed.

The bars above E_K and u in Equation 1.2.2 indicate average values. Average values for speed must be used because not all the molecules are moving at the same speed at any given time. The term \bar{u}^2 is called the *mean-square speed* and is found by taking an average of the squares of the speeds of the molecules. For example:

Gas A: $u = 250 \text{ m s}^{-1}$

Gas B: $u = 300 \text{ m s}^{-1}$

Gas C: $u = 325 \text{ m s}^{-1}$

$$\begin{aligned}\bar{u}^2 &= \frac{(250 \text{ m s}^{-1})^2 + (300 \text{ m s}^{-1})^2 + (325 \text{ m s}^{-1})^2}{3} \\ &= 8.604 \times 10^4 \text{ m}^2 \text{ s}^{-2}\end{aligned}$$

How can this information be used to derive a theory that explains the behaviour of gases? Consider the factors that determine the pressure of a gas in a container. The mass, m , of each molecule and speed, u , of the molecules are two factors. The frequency of collisions—that is, the number of collisions per second—is a third factor.

The frequency of collisions is related to the number of molecules, N , the volume of the container, V , and again, the speed of the molecules, u . Between collisions, the molecules move in straight lines in three-dimensional (3D) space. Only the speed in one dimension is needed since the motion in the other two dimensions is identical. This leads to the basic equation of the kinetic theory of gases:

$$P = \frac{1}{3} \frac{N}{V} m \bar{u}^2$$

From the ideal gas law:

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

it follows that:

$$\frac{1}{3} \frac{N}{V} m \bar{u}^2 = \frac{nRT}{V} \quad (1.2.3)$$

Since m is the mass of one molecule:

$$MM = m \times N_A \text{ and } n = \frac{N}{N_A}$$

Substituting into Equation 1.2.3 and rearranging gives:

$$\bar{u}^2 = \frac{3RT}{MM} \quad (1.2.4)$$

Equation 1.2.4 shows that the mean-square speed of gas molecules is directly proportional to the temperature and inversely proportional to the molar mass. If a gas is heated, the molecules will move faster. If two gases are at the same temperature, the lighter gas molecules move faster, on average, than the heavier gas molecules. Thus, at any given moment, some gas molecules are moving faster and some are moving slower.

The distribution of the speeds of the molecules is governed by the *Maxwell-Boltzmann distribution*. Figure 1.2.2 shows the Maxwell-Boltzmann distribution of molecular speeds for an equal number of moles of four noble gases at 25 °C.

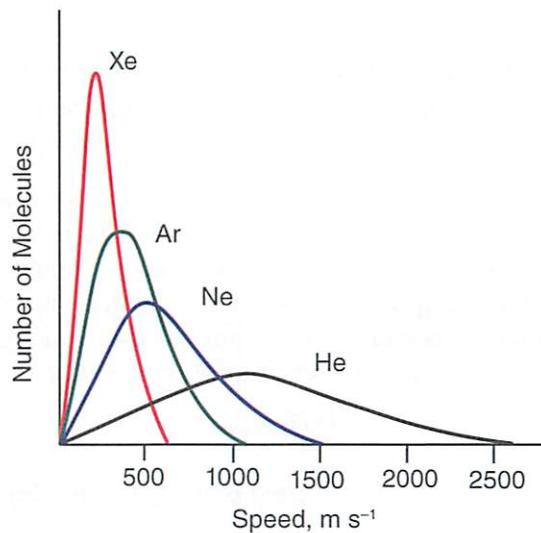


Figure 1.2.2 Maxwell-Boltzmann distribution of molecular speeds.

Root-Mean-Square Speed of Gas Molecules

A more commonly used form of the mean-square speed term is the *root-mean-square* (rms) speed, u_{rms} , which is defined as:

$$u_{\text{rms}} = \sqrt{\bar{u}^2} = \sqrt{\frac{3RT}{MM}}$$

Example 1.2.12. Root-Mean-Square Speed of Gas Molecules

Find the u_{rms} of methane (CH_4) at 300 K.

Solution: $u_{\text{rms}} = \sqrt{\frac{3RT}{MM}}$

$$3RT = (3)(8.314 \text{ kg m}^2 \text{ s}^{-2} \text{ mol}^{-1} \text{ K}^{-1})(300 \text{ K})$$

$$= 7483 \text{ kg m}^2 \text{ s}^{-2} \text{ mol}^{-1}$$

$$MM \text{ of } \text{CH}_4 = 16.04 \text{ g mol}^{-1} = 0.01604 \text{ kg mol}^{-1}. \text{ Therefore:}$$

$$u_{\text{rms}}(\text{CH}_4) = \sqrt{\frac{7483 \text{ kg m}^2 \text{ s}^{-2} \text{ mol}^{-1}}{0.01604 \text{ kg mol}^{-1}}} = 683.0 \text{ ms}^{-1}$$



For two different gases, A and B, at the same temperature (T constant):

$$\frac{u_{\text{rms}}(\text{A})}{u_{\text{rms}}(\text{B})} = \sqrt{\frac{MM_{\text{B}}}{MM_{\text{A}}}}$$

Note that the u_{rms} for two gases is *inversely* proportional to the square root of the ratio of their molar masses.

The units for u_{rms} are metres per second (m s^{-1}), so the molar mass of the gas has to be expressed in kilograms (kg), and the value used for R must be:

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}, \text{ or}$$

$$R = 8.314 \text{ kg m}^2 \text{ s}^{-2} \text{ mol}^{-1} \text{ K}^{-1}$$

Effusion and Graham's Law

Effusion is the flow of gas molecules at low pressures through tiny pores or pin-holes in a container (see Figure 1.2.3). The rate of effusion of a gas is defined as the number of moles of the gas escaping the container per unit of time,

$$r_{\text{eff}} = \frac{n_{\text{eff}}}{t}$$

Scottish chemist Thomas Graham found that lighter molecules effuse more rapidly than heavier ones. In 1846, after extensive experimentation, he formulated what is now known as Graham's law:

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

$$r_{\text{eff}} \propto \frac{1}{\sqrt{MM}}$$

When two gases A and B with equal partial pressures effuse through a porous material or a small hole, Graham's law can be written as:

$$\frac{r_{\text{eff}}^{\text{A}}}{r_{\text{eff}}^{\text{B}}} = \sqrt{\frac{MM_{\text{B}}}{MM_{\text{A}}}} \quad (1.2.5)$$

Because lighter molecules effuse faster than heavier molecules, the gas that emerges from a container is *enriched* in the lighter component.

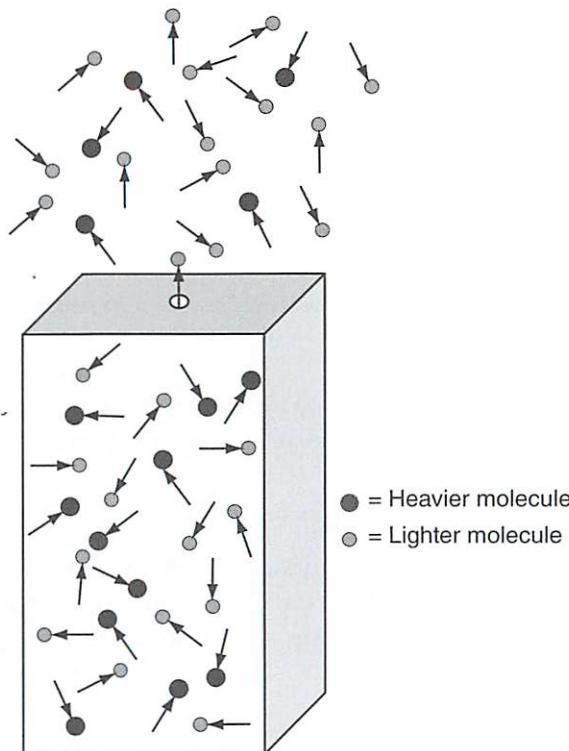


Figure 1.2.3 Effusion of gases through a pinhole in a container.

The quantity $f = \sqrt{\frac{MM_B}{MM_A}}$ is called the *enrichment factor*.

Consider an example. Suppose we have an equimolar mixture of gases A and B with molar masses MM_A and MM_B , respectively. If this mixture is placed into a container with a small pinhole and allowed to effuse for a specific length of time, the gas that escapes will be enriched with the lighter molecules. If gas A is methane, CH_4 ($MM = 16.0 \text{ g mol}^{-1}$), and gas B is oxygen, O_2 ($MM = 32.0 \text{ g mol}^{-1}$), the enrichment factor would be:

$$f = \sqrt{\frac{MM_B}{MM_A}} = \sqrt{\frac{32.0}{16.0}} = \sqrt{2} \approx 1.414$$



Note that the heavier MM (in this case O_2) must be in the numerator of the fraction. This number means that the effused gas stream would have 1.414 times as many methane molecules as oxygen molecules.

Example 1.2.13. Effusion and Enrichment Factor (In-Class Exercise)

The Manhattan Project was a code name for the top-secret WWII-era US-led undertaking to produce the first nuclear weapons. One of the technological challenges in that project was to collect enough nuclear fission material, ^{235}U , by separating it from the more abundant ^{238}U isotope. To this purpose, a mixture of two uranium hexafluoride gases ($^{235}UF_6$ and $^{238}UF_6$) was effused repeatedly. Use the atomic mass of ^{235}U (235.04), ^{238}U (238.05), and F (19.00) to determine the enrichment factor for each effusion.

Example 1.2.14. Effusion and Molar Mass of an Unknown Gas (In-Class Exercise)

Oxygen effuses into an empty (evacuated) cylinder where the pressure reaches 3.0 kPa at 20 °C after 5 minutes. When the experiment is repeated at the same temperature using the same initial number of moles of an unknown gas, the pressure in the cylinder reaches 3.0 kPa after 10 minutes. Determine the molar mass of the unknown gas.

Section 1.2 Practice Problems

1. At what pressure (in kPa) would the density of oxygen be 2.86 g L^{-1} at 50°C ?
2. Assuming ideal gas behaviour, which one of the gases N_2 , CF_2Cl_2 , CO_2 , Kr , and SF_6 would have the lowest density at 0°C and 100 kPa?
3. A gas has a density of 1.20 g L^{-1} at 27°C . If the gas is heated at constant volume in a sealed container, what is the density, in g L^{-1} , at 127°C ?
4. A gas with general formula O_x is found to have a density of 0.189 g L^{-1} at 37°C and a pressure of 10.1 kPa. Find the molar mass of the gas and the value of x .
5. Suppose planet Xebon has an atmosphere composed solely of xenon, Xe . If the pressure at the surface of the planet was 1.01 kPa, and the temperature was 20°C , what would the density (g L^{-1}) of the surface atmosphere be?
6. Two flasks are connected together by a closed valve. One flask contains 1.0 L He at 200 kPa, while the other contains 2.0 L of Ne at 27 kPa. If the temperature remains constant at 27°C , find the final pressure after the valve is opened.
7. A sample of gas contains $\text{N}_2(\text{g})$ at 40.0 kPa, $\text{O}_2(\text{g})$ at 60.0 kPa, and $\text{CO}_2(\text{g})$ at 10 kPa. Calculate the mole fraction of each gas.
8. A mixture of 5.50 g of He, 15.0 g of Ne, and 35.0 g of Kr exerts a total pressure of 100 kPa. What is the partial pressure, in kPa, of He in the mixture?
9. A flask contains a mixture of methane, CH_4 , and ethane, C_2H_6 , at partial pressures of 70.0 and 35.0 kPa, respectively. If the gas temperature is 27°C , what is the average molar mass and density of the mixture?
10. Flasks A and B are connected by a stopcock. Initially, flask A contains 500 mL of O_2 at 100 kPa pressure, while flask B contains 1500 mL N_2 at 50 kPa pressure, both at 25°C . The stopcock is opened and the gases are mixed (but DO NOT react). Determine the partial pressure of each gas after mixing, the total pressure, and the mole fraction of O_2 in the final mixture.
11. A flask contains a mixture of helium, He, and neon, Ne, at 27°C . The partial pressures are 70.0 and 35.0 kPa, respectively. What is the average molar mass, in g mol^{-1} , of the gas mixture?

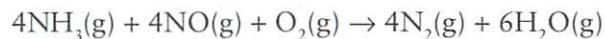


12. An empty balloon is inflated with a mixture of helium and oxygen at 20 °C. He is first added until the volume has reached 10 L at 101 kPa. O₂ is then added until the total volume reaches 30 L, still at 101 kPa. Find, at the final state, the mass and partial pressure of helium, the partial pressure of oxygen, and the mole fraction of each gas.
13. A gaseous mixture of CO and CO₂ exerts a total pressure of 90.0 kPa at 20.0 °C. If the partial pressure of CO is 35.0 kPa, what is the density, in g L⁻¹, of the gas mixture?
14. A 2.00 L bottle initially contains air at 25.0 °C and 110 kPa. “Dry ice” is then placed inside the bottle and the bottle is sealed immediately. If the bottle can withstand a maximum pressure of 500 kPa, what is the minimum amount of dry ice, in grams, required to make the bottle explode at 25.0 °C?
15. A sample of nitrogen gas was collected by water displacement at 27 °C and a pressure of 99.3 kPa. If the volume of nitrogen was 535 mL, what was the mass, in g, of nitrogen gas collected? The vapour pressure of water at 27 °C = 3.6 kPa.
16. If 2.00 L of oxygen gas are collected over water at 50 °C and 94.6 kPa, how many grams of oxygen are obtained? The vapour pressure of water at 50 °C is 12.3 kPa.
17. A chemistry professor’s house is heated by the combustion of methane (CH₄) in air. In one month, he/she used 55.9 m³ of gas, measured at 15 °C and 101.33 kPa. What is the maximum mass of CO₂ (in g) that the professor contributed to the atmosphere in that month by heating the house?
18. If Kr, Xe, O₂, H₂, and N₂ are all at the same temperature, which one has the fastest rms speed? If the rms speed of N₂ is 550 m s⁻¹, what is that of H₂?
19. At the same temperature, what is the value of the ratio:
[average speed of Ar(g)] : [average speed of CH₄(g)]
20. A glass bulb with a small opening initially contains the same number of moles of N₂ and Cl₂. The N₂ is effusing at a rate of 1.5×10^{-4} mol hr⁻¹. What is the effusion rate of the Cl₂?

21. A flask containing a 1:1 mixture (by moles) of O_2 and Cl_2 is connected to a second flask, which is initially empty. There is a very small opening between the two flasks such that, after several hours have elapsed, some of the O_2 and Cl_2 have effused into the second flask. Would the second flask contain more O_2 or more Cl_2 ? What is the ratio of O_2 to Cl_2 in the second flask?

22. Pentane, C_5H_{12} , burns in oxygen to form carbon dioxide and water. What volume (in L) of $O_2(g)$ at 100 kPa and 20 °C is required to react completely with 5.00 g of C_5H_{12} ?

23. Consider the following gas phase reaction:

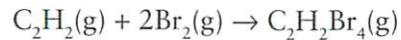


The initial partial pressure of each reactant gas is 60.0 kPa, with the volume and temperature held constant. What is the mole fraction of H_2O in the mixture after the reaction goes to completion?

24. A gaseous compound containing only C, H, and N is mixed with exactly the volume of oxygen required for combustion to CO_2 , H_2O , and N_2 . Burning nine volumes of this mixture of compound and oxygen produces a gaseous mixture of four volumes $CO_2(g)$, six volumes $H_2O(g)$, and two volumes $N_2(g)$, all gas volumes being measured under the same conditions of temperature and total pressure. Write an equation for the combustion reaction, and find the number of volumes of oxygen required for the combustion and the molecular formula of the compound.

25. In a rigid pressure vessel, a mixture was prepared with only $CH_4(g)$ and $O_2(g)$. The mole fraction of the $CH_4(g)$ was initially 0.50. A spark then initiated combustion to $CO_2(g)$ and $H_2O(g)$. What is the mole fraction of $CO_2(g)$ in the vessel after combustion? (Assume all the H_2O remains in the gaseous phase.)

26. A mixture of $C_2H_2(g)$ and excess $Br_2(g)$ is allowed to react completely at constant pressure and temperature:



The total volume of the mixture before reaction is 400 L; the total volume after reaction is 200 L. What was the mole fraction of C_2H_2 in the original mixture before the reaction?

