

Faculty of Science

**Unit 1:
Gases**

CHEM 1523
Principles of Chemistry

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Unit 1: Gases

Overview

In this unit you will study the laws that gases obey, theories that can be used to describe their behaviour, and the chemical and physical properties of the common gases—hydrogen, nitrogen, and oxygen. Most substances can exist in different physical states. The gaseous state, which is much less dense and is highly diffuse, is a convenient starting point in the study of matter since the behaviour of gases can quite easily be described by a simple model. No such model exists for the condensed phases of matter.

In CHEM 1503, *Chemical Bonding and Organic Chemistry*, you were introduced to the belief that matter is discontinuous and particulate in nature. A study of the properties of the gaseous state gives convincing support for this belief. Gases are easily compressed and yet can expand to uniformly occupy the total volume of a container. This is taken as evidence that matter in the gaseous state is made up of very small particles, widely separated from each other.

The gas laws you study will allow you to use fairly simple empirical relationships to calculate various gas parameters. It is also possible to combine stoichiometry problems from CHEM 1503 with gas law calculations.

Another reason to study gases is that we live on a planet that is completely surrounded by a layer of gaseous material—the atmosphere, which is about 80 km thick. The atmosphere is a very complex system; its temperature and pressure vary over a wide range of altitudes. Oxygen and many atmospheric pollutants absorb sunlight and are chemically transformed by this process. Knowledge of gases and gas laws is fundamental if you are to understand the chemical processes occurring around you.

Learning Outcomes

When you reach the end of Unit 1, you should be able to:

- Define the chemical terms introduced in the unit that relate to the gaseous state (e.g., vapour, pressure, atmosphere, ideality, absolute zero, partial pressure).
- Calculate answers to problems involving: (a) relations between the pressure and volume, and between the volume and temperature of an ideal gas; (b) relations between the numbers of molecules (or moles) of a gas and its volume; (c) mixtures of gases and partial pressures; and (d) relative velocities of molecules of different gases.

- Explain the gas laws using the kinetic theory of gases model.
- Calculate the answers to problems involving the ideal gas equation.
- Carry out gas stoichiometry calculations.
- Describe the ideal gas model and state limiting conditions under which the model describes the behaviour of a real gas.
- Use the van der Waals equation in calculations involving real gases.
- Describe the way that temperature and average velocity/kinetic energy are related by sketching general Maxwell-Boltzmann distribution curves at high and low temperatures.
- Describe physical and chemical properties of hydrogen, nitrogen, and oxygen, and some of their common compounds.

Textbook Readings

As you progress through the learning units, you will be directed to read specific sections of your textbook.

Study Section 1.5 of your textbook. This section will provide an introduction to the gaseous state of matter. You are already aware of some of the macroscopic properties of matter, such as the compressibility of gases, or that liquids take the shape of the container in which they are held. In this unit you will also consider some of the microscopic properties of matter. These properties can be deduced from models, and the models are then used to build up working theories.

Substances That Exist as Gases

Study Section 5.1 of your textbook. You should know those elements that exist as gases under normal conditions of temperature and pressure. You should also know that, except for the noble gases (i.e., He, Ne, Ar, Kr, Xe, and Rn) that are monatomic, the remaining gaseous elements normally exist as diatomic molecules. You do not have to memorize the compounds listed in Table 5.1 in your textbook. Generally in the textbook and in the units, a gaseous compound (or element) will be described by a “g” contained in brackets, e.g., $\text{CO}_2(\text{g})$.

The terms **gas** and **vapour** are often used interchangeably although they are not exactly the same. A gas is normally in the gaseous state at room temperature and pressure, while a vapour is the gaseous form of a substance that is normally a liquid or a solid at room temperature and pressure. Thus, we could say “nitrogen gas,” but we would use the term **water vapour**.

Pressure of a Gas

Study Section 5.2 of your textbook. Pressure is an easily measured property of gases. There are various units of pressure, but the unit “atmosphere” (atm) is still commonly used in chemistry, despite the fact that it is not an SI (metric) unit. The SI unit of pressure is the pascal (Pa), and

$$Pa = N \times m^{-2} = kg \times m \times s^{-2} \times m^{-2} = kg \times m^{-1} \times s^{-2}$$

Generally, chemists still use atmospheres instead of pascals for their measurements of gas pressure. You will find the atm used in your textbook and in almost all other textbooks and chemical literature.

You can always convert atm to SI units, or to the other commonly used pressure units in chemistry (mm of Hg and torr), by using the conversion factors

$$1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ torr} = 101\,325 \text{ Pa} = 101.325 \text{ kPa}$$

Conversion factors such as this will always be given to you, or you can look them up inside the back cover of your textbook. You do not need to memorize them.

Throughout this course, we will use both atmospheres and kilopascals, and you should be able to use either unit. In fact, since you will always be given the conversion factors involved, and you should be able to use atmospheres, torr, mm of Hg, and kPa.

Work through Examples 5.1 and 5.2 and their practice exercises in your textbook. The answers to the practice questions are at the very end of the chapter.

The Gas Laws

Study Section 5.3 of your textbook.

Boyle's Law

The relationship between pressure and volume, assuming a constant temperature, is known as Boyle's law. You are probably already aware that an increase in volume will lead to decreased pressure, and that a decrease in volume will lead to an increased pressure. This is known as an **inverse proportionality** and can be written as

$$PV = \text{constant}$$

Figure 5.7 in your textbook expresses this idea graphically. Boyle's law has many practical applications, as shown by the following example.

Problem: A scuba diver with a lung capacity of 5.00 L is at a depth in the ocean where the water pressure is 5.00 atm.

The diver, suddenly glimpsing an enormous shark, panics, takes a lungful of air, and shoots to the surface while still holding his breath. To what volume must his lungs expand at the surface?

Solution: If you treat this problem as a Boyle's law calculation,

$$\begin{array}{ll} P_1 = 5.0 \text{ atm} & V_1 = 5.0 \text{ L} \\ P_2 = 1.0 \text{ atm} & V_2 = ? \end{array}$$

Then,

$$P_1 V_1 = P_2 V_2 \quad V_2 = \frac{P_1 V_1}{P_2} = \frac{5.0 \text{ atm} \times 5.0 \text{ L}}{1.0 \text{ atm}} = 25 \text{ L}$$

Of course, it is biologically impossible for your lungs to expand to 25 L without problems. The damage done by such an "air embolism" can be fatal, and it would be in this case. The diver should have exhaled as he surfaced, and kept his rate of ascent the same as that of his bubbles.

The Law of Charles and Gay-Lussac

This law, relating volume and temperature of a gas, is often just called Charles' law. It is from this law that the concept of an absolute zero of temperature first arose. Figure 1.1 in this unit shows the results of graphing the volumes of different samples of different gases against the temperature. Extrapolation of each straight line gives the same value (-273.15°C) for the point at which the gas theoretically would have zero volume.

Figure 5.9 in your textbook is similar to this graph but involves different pressures. Charles' law states that a gas contracts by $1/273$ (to be really precise you would use $1/273.15$) of its volume for each Celsius degree of cooling. From this it follows that, if a gas is cooled from 0°C to -273°C , it would contract by $273(1/273)$ or 100% of its volume. This leads to (but does not prove) the concept of an absolute zero. You should note that the temperature in $^\circ\text{C}$ (t) is always converted to the Kelvin scale (T) before using it in any gas law calculation.

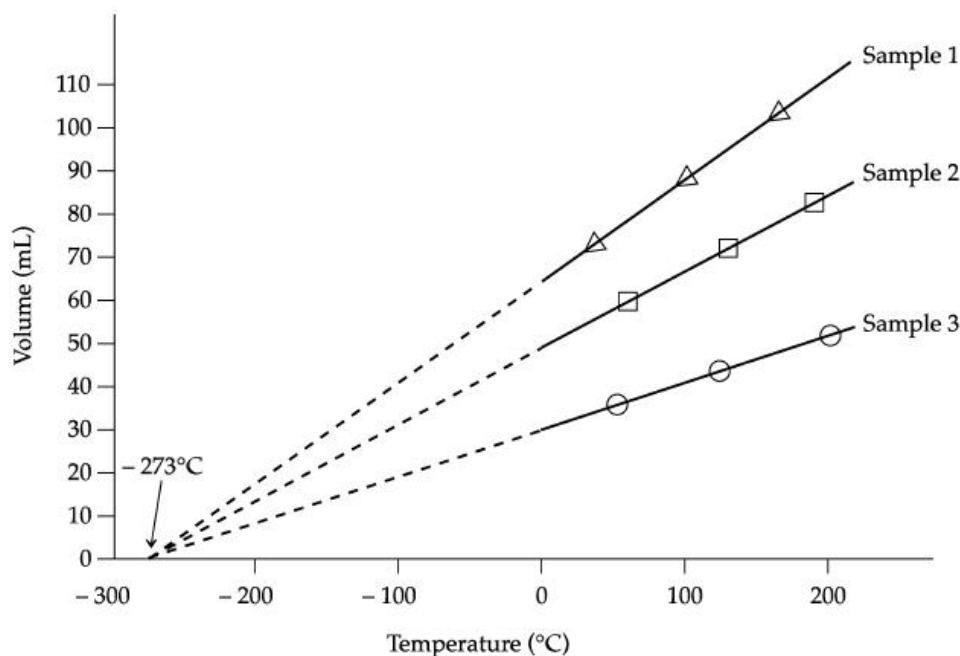


Figure 1.1: Charles' law extrapolation to absolute zero. Data for three different samples of gases have been plotted as volume against temperature, with pressure held constant. For each example, the data points are on a straight line. On extrapolation, each line intersects the temperature axis at a point where there is zero volume, at -273°C .

Avogadro's Law

Avogadro's law introduces the fourth factor in gas measurements—the amount of gas. This is usually given as n , the number of moles of the gas. At constant temperature and pressure, the volume of a gas is directly proportional to the number of moles of the gas.

The Ideal Gas Equation

Study Section 5.4 of your textbook and work through Examples 5.3 and 5.4, as well as the accompanying practice exercises, making sure that you understand them.

Using $PV = \text{constant}$ (Boyle's law), $V/T = \text{constant}$ (Charles' law) and $V/n = \text{constant}$ (Avogadro's law) together, you can show that PV/nT is always a constant. This constant is given the symbol R and is known as the **universal gas constant**, or the **ideal gas constant**. The relationship is usually written as

$$PV = nRT$$

and is known as the **ideal gas equation**. You should memorize this equation since you will be using it often. It is called the *ideal* gas equation because it is a limiting equation, that is, it is valid only at the limit of zero density (zero pressure and high temperature).

Later in this unit you will encounter the reasons for the limits on the ideal gas equation. The value of R depends on the units of pressure and volume that you are using.

$$R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

when pressure is in atmospheres and volume is in litres, or

$$R = 8.314 \text{ L kPa mol}^{-1} \text{ K}^{-1}$$

when pressure is in kilopascals and volume is in litres. In later parts of this course, you will encounter a value of $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$. If you define pressure units and volume units using the SI methods, you can see that the product of pressure and volume has the dimensions of energy. The SI definition (where pressure is multiplied by volume) is

$$\text{kg m}^{-1} \text{ s}^{-2} \times \text{m}^3 = \text{kg m}^2 \text{ s}^{-2} = \text{J (joule)}$$

You need not memorize any of these values of R . You can simply look them up at the back of your textbook. You will be given these values when you write an exam. What you do have to know is which value of R to use, and this value depends on the units in the problem. Almost all gas law calculations use $R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$ as pressure units are usually given in atmospheres (or mm Hg, or torr, and then converted to atmospheres). Although you do not have to memorize $R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$, you will probably find that, after using it many times, you have memorized it.

The ideal gas equation can be used to derive all other relationships involving pressure, volume, temperature and number of moles. $PV/nT = \text{constant}$ can be expressed as

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

where n_1 means the number of moles in volume V_1 at pressure P_1 and temperature T_1 , and n_2 means the number of moles in volume V_2 at pressure P_2 and temperature T_2 . If n and T are held constant,

$$P_1 V_1 = P_2 V_2$$

which is Boyle's law. If P and n are held constant, the expression becomes

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

which is Charles' law. If P and T are held constant, the result is

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

or Avogadro's law. By holding constant any two parameters, the relationship between the other two can be shown. For example,

$$\frac{P_1}{n_1} = \frac{P_2}{n_2}$$

at constant volume and temperature, or

$$n_1 T_1 = n_2 T_2$$

at constant pressure and volume.

You should memorize that one mole of any gas at STP (standard temperature and pressure) occupies 22.4 L (this is the molar volume). Now work through Examples 5.5, 5.6, and 5.7 and their practice exercises.

Density and Molar Mass

By manipulating the ideal gas equation, it is possible to determine the density of a gas. Further, if you are given the density of a gas at known conditions, you can determine the molar mass of the compound. These types of calculations are demonstrated in your textbook in Examples 5.8, 5.9, 5.10 and their practice exercises. Examples 5.9 and 5.10 include an empirical formula determination you learned in CHEM 1503. In this instance, the molecular formula is calculated using the molar mass as determined by the gas laws.

Gas Law Stoichiometry

The gas laws and, in particular, the ideal gas equation are often used to determine volumes of gases produced or used in chemical reactions. The relationships that you need for this type of calculation are summarized in Figure 1.2 of this unit.

Study Section 5.5 in your textbook. Work through Examples 5.11, 5.12 and 5.13 and the practice exercises. Notice how, in each case, it is important that you determine the number of moles of reactant (whether a solid or a gas), use the stoichiometry of the equation to determine the number of moles of product, and then convert to mass or volume of product.

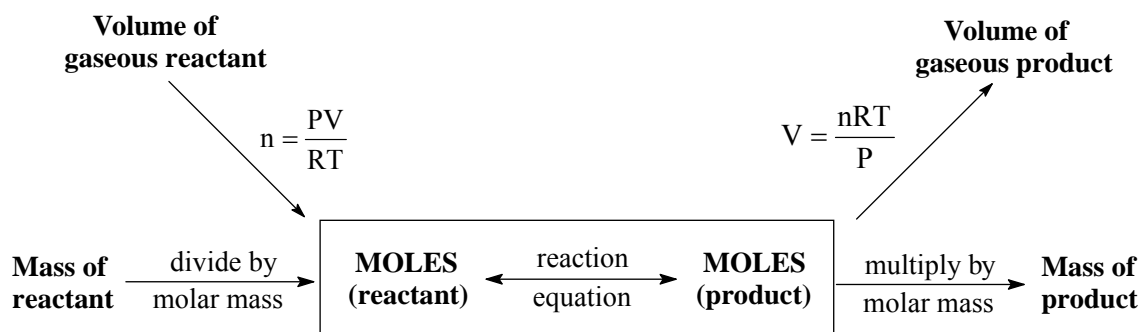


Figure 1.2: Stoichiometric and gas law relationships

Dalton's Law of Partial Pressure

Study Section 5.6 in your textbook. Dalton's law says that the total pressure exerted by a mixture of gases is due to the sum of pressures exerted by each gas. You often have to work out the partial pressure of each gas (the partial pressure is the pressure that the gas would exert if it alone was present in the same volume). The partial pressure of a gas is proportional to the mole fraction of the gas present. The concept of partial pressure is used when you discuss the amount of oxygen in air. At a pressure of one atmosphere, you can assume that air contains 0.78 moles of nitrogen, 0.21 moles of oxygen, and 0.01 moles of argon. The partial pressure of oxygen in air is then mole fraction $O_2 \times$ total pressure, that is,

$$\frac{0.21}{0.21 + 0.78 + 0.01} \times 1 \text{ atm} = 0.21 \text{ atm}$$

Our bodies need a partial pressure of oxygen of about 0.2 atm. Consequently, if a lot of extra inert gas is present, the partial pressure of O_2 drops. You could eventually suffocate, even if the total number of molecules of O_2 remains unchanged.

Our atmosphere contains varying amounts of water vapour depending on climate and the region of the world. The term *relative humidity* is defined as the amount of water vapour in the air at a specific temperature compared to the maximum amount of water vapour that can be contained in the air at that temperature. Relative humidity is usually expressed as a percentage, that is

$$\text{relative humidity} = \frac{P_{H_2O}}{P_{H_2O(\text{sat})}} \times 100\%$$

Where P_{H_2O} is the pressure of the water vapour in the air at temperature T, and $P_{H_2O(\text{sat})}$ is the pressure when the air is saturated with water vapor. On hot days, the saturated vapour pressure of water is much higher than on cold days.

Therefore, 95% relative humidity at 35°C involves a much higher amount of water vapour in the air than 95% relative humidity at 15°C.

The best way to understand the concepts of partial pressure and mole fraction is to use them in a calculation.

Problem: A mixture of gases contains 10.0 g of Ne, 18.5 g of CO₂, and 15.0 g of N₂. The total pressure of the mixture is 1.15 atm. Calculate the partial pressure of each gas.

Solution: First you have to find the mole fraction of each gas. To do this, convert the mass of each gas into moles.

$$\text{Ne: } \frac{10.0 \text{ g}}{20.2 \text{ g mol}^{-1}} = 0.495 \text{ mol Ne}$$

$$\text{CO}_2: \frac{18.5 \text{ g}}{44.0 \text{ g mol}^{-1}} = 0.420 \text{ mol CO}_2$$

$$\text{N}_2: \frac{15.0 \text{ g}}{28.0 \text{ g mol}^{-1}} = 0.536 \text{ mol N}_2$$

Therefore, the mole fraction of Ne is:

$$\frac{\text{moles Ne}}{\text{total number of moles of gas}} \left(\text{or } \frac{n_{\text{Ne}}}{n_{\text{total}}} \right) = \frac{0.495}{1.451} = 0.341$$

Similarly, the mole fraction of CO₂ is

$$\frac{0.420}{1.451} = 0.289$$

and the mole fraction of N₂ is

$$\frac{0.536}{1.451} = 0.369$$

Note: You can check at this point that you have not made a mistake. The sum of the mole fractions should equal 1.

Check: 0.341 + 0.289 + 0.369 = 0.999 or 1

Now use (partial pressure) = (mole fraction × total pressure) for each gas.

$$P_{\text{Ne}} = n_{\text{Ne}} \times P_{\text{total}} = 0.341 \times 1.15 \text{ atm} = 0.392 \text{ atm}$$

$$P_{\text{CO}_2} = n_{\text{CO}_2} \times P_{\text{total}} = 0.289 \times 1.15 \text{ atm} = 0.332 \text{ atm}$$

$$P_{\text{N}_2} = n_{\text{N}_2} \times P_{\text{total}} = 0.369 \times 1.15 \text{ atm} = 0.424 \text{ atm}$$

You can check again by making sure that Dalton's law is obeyed:

$$P_{\text{total}} = P_{\text{Ne}} + P_{\text{CO}_2} + P_{\text{N}_2} = 0.392 + 0.332 + 0.424 = 1.15 \text{ atm}$$

It is important that you can use the following relationships.

$P_{\text{total}} = P_1 + P_2 + P_3 + \dots + P_n$	Dalton's law
$n_X = \frac{\text{moles of gas X}}{\text{total number of moles of gas}}$	definition of mole fraction
$P_X = n_X \times P_{\text{total}}$	partial pressure of gas X equals mole fraction of gas X times total pressure

Make sure you go over Example 5.14 and the practice exercise in your textbook. A very common use of Dalton's law is shown in Example 5.15. If a gas is "wet" (i.e., collected over water), you must "dry" it by taking into account the vapour pressure of the water.

The pressure given is due to the pressure of the gas and the pressure of the water vapour. To dry the gas, subtract the pressure due to the water vapour at that particular temperature.

$$P_{\text{dry gas}} = P_{\text{wet gas}} - P_{\text{H}_2\text{O}}$$

There is nothing magical about this "drying step." In the presence of water vapour, the partial pressure of every other gas is lowered, and this is why you have to subtract. Now try the practice exercise from Example 5.15 in your textbook.

Table 5.3 in your textbook shows vapour pressures of water at various temperatures. You are not expected to remember these. You can either look them up or they will be given to you.

At this stage it is important that you do some gas law calculations on your own, before continuing with the rest of the unit. Turn to the Suggested Supplementary Exercises at the end of this unit for instructions on where to find some appropriate problems.

Kinetic Molecular Theory of Gases

Study Section 5.7 in your textbook. The kinetic theory of gases can be used as a model to visualize what is happening on a molecular level in a gas. Using this model, you can deduce each of the gas laws exactly.

Application to Gas Laws

The overall pressure exerted by a gas is due to the collisions of the gas molecules with the walls of the container. You may know from your study of physics that a definition of pressure can be written as

$$\text{Pressure} = \text{force per unit area.}$$

In SI units, pressure is defined as $\text{kg m}^{-1} \text{s}^{-2}$. This fact alone tells you that a change in any of these three base SI quantities (mass, length or time) causes a change in the pressure.

If there are more collisions per unit of time, or if heavier molecules are involved in these collisions, or if the distance between the container walls decreases, the pressure increases.

If the volume of the container increases, the area of the container walls increases and the distance that molecules have to travel before hitting the container wall increases. Molecules will therefore collide less frequently with the container walls. So an increased volume leads to fewer collisions and a decreased pressure. This is, of course, Boyle's law.

One important consequence of the kinetic molecular theory is that the average kinetic energy of all molecules in a gas is proportional to the temperature (K) of the gas. If you increase the temperature of a gas, the average kinetic energy ($\frac{1}{2}mv^2$) and, hence, the average velocity of the molecules will increase. As the molecules go faster they will hit the wall more often. If you now wanted to keep the pressure constant, you would have to expand the volume of the container so that the faster molecules had to travel further. Overall, to keep the pressure constant, increased temperature means an increased volume—this is Charles' law.

You can also rationalize Avogadro's law using the kinetic molecular theory of gases. If you increase the number of moles (and therefore molecules) of the gas while keeping the temperature (average velocity of the molecules) constant, then the only way to maintain a constant pressure is to increase the volume. This requires that the larger number of molecules travel farther between collisions.

The other relationships summarized in the ideal gas equation can be derived from simple reasoning like this. You should see if you can use the kinetic molecular theory of gases to deduce the relationship between: (a) the number of moles, n , and the pressure, P ; (b) the number of moles, n , and the temperature, T ; and (c) the pressure, P , and temperature, T . Your result should agree with the mathematical expression

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

The kinetic theory of gases can also be used to explain Dalton's law of Partial Pressures. As different gas molecules do not exert forces on each other except when they collide, their partial pressures can be calculated as if each gas occupied the volume on its own. Heavier gas molecules move more slowly than lighter gas molecules at the same temperature since both have the same average kinetic energy ($\frac{1}{2}mv^2$). The heavier molecules therefore collide less often with the container walls, but the collisions have greater impact.

An understanding of the kinetic theory of gases is extremely helpful when you do gas law calculations. It is easy to use a formula like $PV=nRT$ or

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

But it is also easy to make a mistake or use a wrong value when you substitute. You should get into the habit of looking at your answer to a gas law calculation and checking mentally that it makes sense according to the kinetic theory of gases. Here is an example of such a calculation.

Problem: A gas kept in a constant volume container has a pressure of 1.60 atm at 25.0°C. The temperature is raised to 79.0°C. What is the new pressure of the gas?

Solution: Use $PV=nRT$, or

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

Since n , R , and V are all constant in this case, the ratio P/T is also constant, or

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

Now, $P_1 = 1.60$ atm, $P_2 = ?$, $T_1 = 298$ K, and $T_2 = 352$ K,

$$\text{so } P_2 = \frac{P_1 \times T_2}{T_1} = \frac{1.60 \text{ atm} \times 352 \text{ K}}{298 \text{ K}} = 1.89 \text{ atm}$$

You should then look at your answer in terms of the kinetic theory. Your thoughts might occur something like this: "I have to increase the temperature, so the molecules—a constant number of them—will move faster and hit the wall more often. The walls cannot expand since the container has a constant volume, so more collisions on the walls means increased pressure. This is in line with what I calculated." Relating your gas law calculations and kinetic theory of gases in this manner will increase your understanding of them both.

The Maxwell-Boltzmann Equation

Figure 1.3 in this unit is a graphical representation of the complicated relationship known as the Maxwell-Boltzmann equation. This equation relates number of molecules to their kinetic energy and, thus, to their molecular speed. This figure is sometimes known as the Boltzmann distribution. It can also be used to demonstrate other molecular concepts such as evaporation. If point E on the x -axis represents the kinetic energy required by a molecule to escape from the surface of a liquid, then all molecules with kinetic energy greater than E, and at the surface, will be able to evaporate. At higher temperatures (T_2 and T_3 in Figure 1.3), more molecules have a kinetic energy greater than E and, therefore, more rapid evaporation occurs at higher temperatures. If the molecules with kinetic energy greater than E are removed, the average kinetic energy of the remaining molecules decreases. Since kinetic energy is proportional to temperature, the unevaporated liquid experiences a cooling—a phenomenon known as “evaporative cooling.”

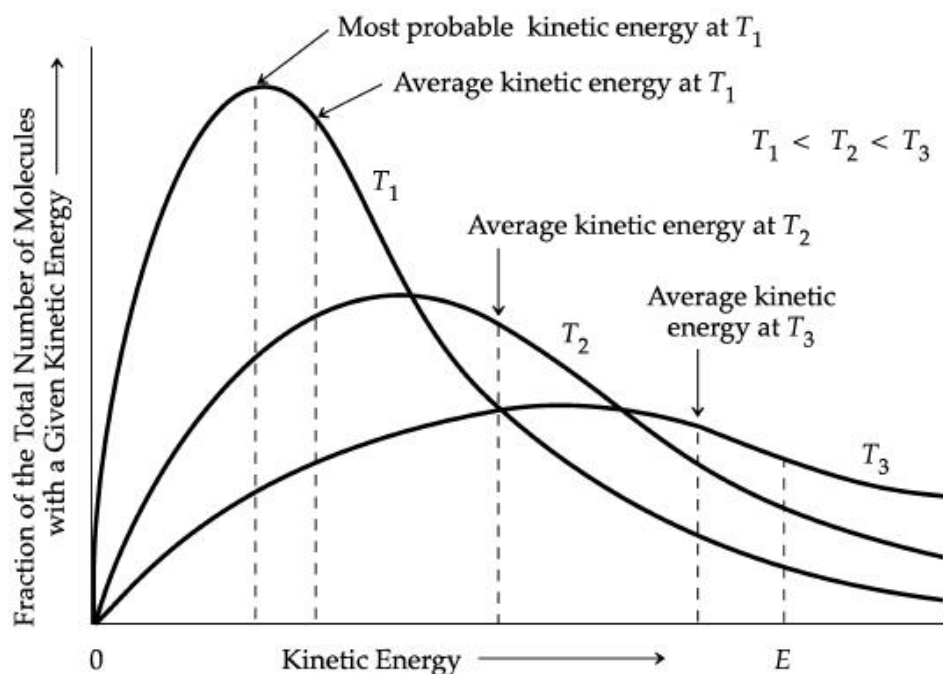


Figure 1.3: Maxwell-Boltzmann distributions of molecular kinetic energy. The mole fraction of molecules having a particular kinetic energy is graphed as the dependent variable (y —or vertical axis) against the kinetic energy as the independent variable (x —or horizontal axis). E is the kinetic energy required to overcome attractive forces of other molecules in the liquid, that is, the energy necessary for evaporation. Note the different shapes of the curves as the temperature changes. $T_1 < T_2 < T_3$. At higher temperatures, a larger fraction of molecules has a kinetic energy greater than E. Similar curves are obtained if you graph molecular velocity instead of kinetic energy as the independent variable (horizontal axis).

Root-mean-square speeds (u_{rms}) at different temperatures can be calculated using the relationship

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

as shown in Example 5.16 in your textbook.

Graham's Law of Diffusion and Effusion

Effusion and diffusion are processes that depend on the molecular speed of a gas. The two terms are sometimes used interchangeably. They shouldn't be. Effusion occurs when a gas passes through a hole in a container that is empty. Diffusion describes the process of a substance spreading through another medium. Specifically for gases, diffusion usually implies mixing of one gas throughout another. Both effusion and diffusion follow Graham's law:

$$\frac{\text{rate (of diffusion or effusion) of gas A}}{\text{rate (of diffusion or effusion) of gas B}} = \sqrt{\frac{\text{density of gas B}}{\text{density of gas A}}}$$

However, at constant temperature and pressure, the density of a gas is directly proportional to its molar mass, M . Graham's law is often written as

$$\frac{\text{rate}_A}{\text{rate}_B} = \sqrt{\frac{\text{molar mass}_B}{\text{molar mass}_A}}$$

and is another method of determining the molar mass of an unknown gas.

A macabre example of the usefulness of Graham's law is given in the following example, known as "the die laughing calculation."

Problem: An inept researcher, who had set up a system of remote controlled stopcocks on gas cylinders stored at one end of the laboratory, inadvertently pushed the button that allowed a small opening in two of the cylinders. One cylinder contained hydrogen cyanide (HCN) gas, a deadly poison, and the other cylinder contained dinitrogen oxide (N_2O)—also known as "laughing gas." Did the researcher, sitting at the far end of the laboratory, die laughing?

Solution: Assume that both gases had the same distance to travel as they diffused towards the researcher.

$$\text{molar mass HCN} = 27.0 \text{ g mol}^{-1}$$

$$\text{molar mass N}_2\text{O} = 44.0 \text{ g mol}^{-1}$$

Substituting into Graham's law,

$$\frac{\text{rate of diffusion of HCN}}{\text{rate of diffusion of N}_2\text{O}} = \sqrt{\frac{\text{molar mass N}_2\text{O}}{\text{molar mass HCN}}} = \sqrt{\frac{44.0 \text{ g mol}^{-1}}{27.0 \text{ g mol}^{-1}}} = 1.28$$

Since HCN diffuses 1.28 times faster than N₂O, it will reach the researcher first, so **no, he will not die laughing!**

When you are doing Graham's law calculations, remember that "rate" is not the same thing as "time." That is,

$$\text{rate} = \frac{\text{distance}}{\text{time}}$$

In some problems you will be asked how long it takes for a particular gas to diffuse. Use the rate of diffusion in Graham's law to determine the rate, and then calculate the time taken.

Deviation from Ideal Behaviour

Study Section 5.8 in your textbook. You should note that there is no such thing as an ideal gas! If you imagine that a mythical gas obeyed the gas laws absolutely, then your mythical gas would be ideal. At pressures around 1 atm and at room temperature or higher, the error involved in assuming ideal behaviour in real gases is small. However, at high pressures such as those often found in industrial processes, gas behaviour is nonideal.

At atmospheric pressure and room temperature, most gases approximate ideal behavior. Outside these limits gases depart markedly from ideality. Figure 5.22 in your textbook shows the variation from ideality of methane, hydrogen, and ammonia. Figure 1.4 in this unit also shows how pressure and temperature affect the deviation from ideality of particular gases.

- (a) The pressure-volume product as a function of pressure at 0°C for H₂, N₂, O₂, and CO₂. Notice the marked departure from ideality at high pressures for H₂, N₂, and O₂ and for the larger CO₂ molecule at high and low pressures.
- (b) Compressibility factor (PV/RT) as a function of pressure for 1 mole of N₂ at different temperatures. At lower temperatures, where intermolecular attractions have more effect, the departure from ideality is more pronounced.

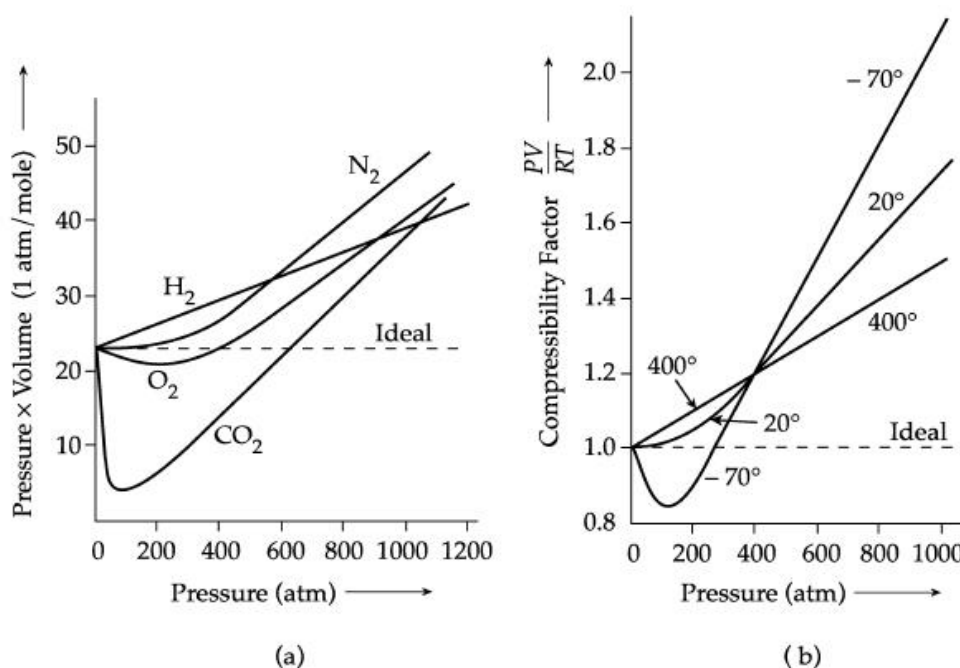


Figure 1.4: Deviations from ideality in real gases.

The two main factors that differentiate real gases from the model of an ideal gas are that molecules of real gases *do* have a volume and *are* attracted to one another. At low temperatures, molecules of real gases do not have enough kinetic energy to overcome intermolecular attractions, and the gas deviates from ideality. At high pressures, the actual volume occupied by molecules of gases (as opposed to the volume, V , where these molecules are contained) becomes significant. You should note that, in gas equations, V always refers to the space where gas molecules are free to move; this space is less than the volume of the container. Real gases act in a less than ideal manner at low temperatures and high pressures. You can see this graphically in Figure 1.4.

One method of correcting for the nonideality of a gas is the van der Waals equation:

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

The van der Waals constants are a and b . These vary depending on the gas involved. You are not expected to memorize any of these van der Waals constants. You can look them up in Table 5.4 of your textbook, or they will be given to you. Work through Example 5.18 in your textbook. This example shows how you use the van der Waals equation in a calculation. Try the practice exercise as well. You do not normally need to use the van der Waals equation. If you are expected to use it, you will be told in the question or given the constants.

Some Common Gases

Unit 1 comes to a close with a discussion of the physical properties, chemical properties, and some compounds of three common gases—hydrogen, nitrogen, and oxygen. This may be your first encounter with what is often called systematic inorganic chemistry. You should be familiar with electronic configuration designations (e.g., $1s^2$ or $1s^2 2s^2 2p^3$) and chemical bonding from your CHEM 1503 course.

We end this topic with a selection of textbook readings that cover the most important information that you should know about these three gases. Start by reading Section 22.1 in your textbook.

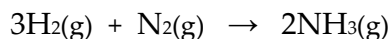
Hydrogen

Section 22.2 in your textbook discusses hydrogen. You do not need to know all of this material. You should know at least one laboratory and one commercial preparation of hydrogen gas. You should know the term **binary hydride** and be able to distinguish between an ionic and a covalent hydride. Study the relevant parts of Section 22.2. You may be interested in reading about metallic hydrogen in the **Chemistry in Action** box. There is also considerable current interest in the use of hydrogen gas as a vehicle fuel to reduce the demand on oil reserves and the amount of carbon dioxide produced.

Nitrogen

Both nitrogen and phosphorus are discussed in Section 22.4 in your textbook, but you need only study the first part of that discussion on nitrogen. Despite the fact that nitrogen in its elemental form, N_2 , is an extremely inert material, nitrogen is widespread in nature. You may want to read about the nitrogen cycle in Section 20.1, in the textbook chapter on the atmosphere. Notice the names of the compounds of nitrogen given in Table 22.2 in your textbook. These are generally trivial names (International Union of Pure and Applied Chemistry, IUPAC, names are sometimes given in brackets). You do not have to memorize all these names, but you should know ammonia, nitrous and nitric acid, and of course be able to give a formula from an IUPAC name.

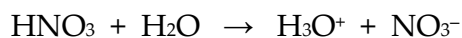
Ammonia, NH_3 , is made from hydrogen and atmospheric nitrogen by a reaction also known as the Haber process.



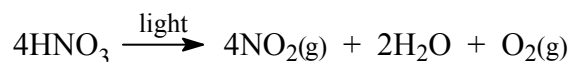
This is an important reaction because it is a chemical means of fixing nitrogen from the air into a form that can be utilized by plants.

You can read about the Ostwald process for producing nitric acid in Section 13.6 of your textbook, but you do not need to memorize details. Continue with Section 22.4 in your textbook to read about the three common oxides of nitrogen, N_2O , NO , and NO_2 , remembering that the details of their bonding and structure are not necessary at this point.

Nitric acid is a strong acid, one that totally ionizes in water.



Concentrated nitric acid is about 67% by weight HNO_3 . The remaining 33% is water. In the laboratory nitric acid is often kept in brown bottles. This is because nitric acid undergoes a slow decomposition in the presence of light.



The dissolved NO_2 gas that is produced gives the solution a yellow or brown colour, often considered characteristic of nitric acid. There is often a brown vapour above liquid HNO_3 . Nitric acid is a powerful oxidizing agent and dissolves nearly all metals. The few that do not dissolve in HNO_3 are platinum, gold, iridium, and rhodium. These metals are often known as the noble metals. You may have heard of the acid mixture, *aqua regia*, a mixture of two or three parts of concentrated hydrochloric acid, HCl , to one part concentrated HNO_3 . *Aqua regia* (literally, royal water) will dissolve even those metals resistant to concentrated HNO_3 alone, and is the only solvent able to dissolve gold.

Oxygen

Oxygen and sulphur are described in Section 22.5 in the textbook. Study those portions of this section that relate to the discussion below. You should also know a laboratory and a commercial method for preparing oxygen.

Oxygen can exist in two different elemental forms or **allotropes**. O_2 is the more common and more stable form. Ozone, O_3 , is the less common and the less stable allotrope. Do not worry about the bonding in, and the structure of, the O_3 molecule for this discussion, but read about the preparation and uses of ozone. You have probably read about the ozone layer in the upper atmosphere. The natural production of this layer and its possible destruction are discussed in detail in Section 20.3 in the “Chemistry in the Atmosphere” chapter in your textbook.

Although it is not part of this unit on gases, you may want to read about the other nonmetallic elements described in the textbook chapter “Nonmetallic Elements and Their Compounds”: carbon, silicon, phosphorus, sulfur, and the halogens. There is much interesting and useful chemistry covered here.

Self-Assessment

Having reached the end of Unit 1, you should be able to:

- Define the chemical terms introduced in the unit that relate to the gaseous state (e.g., vapour, pressure, atmosphere, ideality, absolute zero, partial pressure).
- Calculate answers to problems involving: (a) relations between the pressure and volume, and between the volume and temperature of an ideal gas; (b) relations between the numbers of molecules (or moles) of a gas and its volume; (c) mixtures of gases and partial pressures; and (d) relative velocities of molecules of different gases.
- Explain the gas laws using the kinetic theory of gases model.
- Calculate the answers to problems involving the ideal gas equation.
- Carry out gas stoichiometry calculations.
- Describe the ideal gas model and state limiting conditions under which the model describes the behaviour of a real gas.
- Use the van der Waals equation in calculations involving real gases.
- Describe the way that temperature and average velocity/kinetic energy are related by sketching general Maxwell-Boltzmann distribution curves at high and low temperatures.
- Describe physical and chemical properties of hydrogen, nitrogen, and oxygen, and some of their common compounds.

Practice Exercise 1

Finish working through Unit 1 before starting this practice exercise which is found listed under the Practice Exercises section of course. The material in this unit is integrated throughout the practice exercises. The solutions to these problems will be provided once you have completed this practice exercise.

You may first want to try some of the supplementary exercises suggested under the next heading. However, if you feel that you have a reasonable understanding of the material, you can begin the practice exercise immediately. If you have no difficulties with this practice exercise, begin Assignment 1. If you feel that you need more practice, go to the Suggested Supplementary Exercises.

You should make a serious attempt to solve the practice exercise problems by yourself, using as a guide similar exercises from the textbook and from this unit. If your attempt is serious, you will learn a lot from the worked solutions in the Solutions to Practice Exercise 1 section of the Course Units.

Suggested Supplementary Exercises

At the end of each chapter in your textbook are further exercises on the material covered. We suggest that you do as many of these exercises as necessary. Doing such problems helps you understand and apply the principles involved in the concepts discussed. Fully worked solutions for most of the following exercises are given in the *Student Solutions Manual*. Most selected exercises at the ends of the chapters have their answers in the back of the textbook, or a solution method is described in the *Student Solutions Manual*.

You should make a serious attempt to solve a problem by yourself before looking at a worked solution.

From Chapter 5:

5.14, 5.18, 5.20, 5.22, 5.24, 5.30, 5.32, 5.34, 5.36, 5.38, 5.42, 5.44, 5.46, 5.48, 5.50, 5.56, 5.60, 5.62, 5.66, 5.77, 5.84, 5.86, 5.90, 5.94, 5.98, 5.100, 5.104

Assignment 1

Now refer to your *Assignments* and complete Assignment 1. Consult your Course Guide for the week this assignment is due. Send the assignment to your Open Learning Faculty Member.

You may send the assignment to your Open Learning Faculty Member using the assignment tool in Blackboard or by mail with a Marked Assignment Form.

Be sure to keep a copy of the assignment—it will be useful if you wish to discuss your work with your Open Learning Faculty Member.