

Chapter 15. Gases

15.1. The Gaseous Phase

The nature and behavior of gases (Latin, *chaos*) has been a subject of interest in every age of science. Not only is the study of gases important from a practical point of view (consider breathing, flying or air pollution), but forms a fascinating subject from a conceptual viewpoint (consider the invisible, yet forceful wind). Hero's toy steam engine of the Golden age of Greek science was developed from investigating the power of steam produced by boiling water. The steam engine powered the industrial revolution of the Nineteenth Century. Antoine Lavoisier determined the law of conservation of matter only after considering the role of gases in chemical reactions. John Dalton developed his atomic theory of matter after investigating the behavior of gases under controlled conditions. One of the early quantitative Renaissance statements of physical science was Robert Boyle's law of gases. The great reputation that science enjoys in our century derives, in part, from the eminently successful theoretical insights into the nature of the gaseous phase developed during the Nineteenth Century.

The good news is that the basic laws of behavior of simple gases are quite simple, at least when expressed mathematically. The bad news is that there are so many laws. Most students don't have much trouble with the calculational part of gas law problems. What they do have trouble with is figuring out *which* equation to use for a given problem. In this chapter you will learn a simple procedure for identifying which law applies to a given situation, and you will learn about algorithms for the laws to the situation.

15.2. Gas Laws

Gas laws describe the *physical* behavior of gases under *non-reactive* conditions, as distinct from the *chemical* behavior of *reactive* substances. Gas laws find a place in chemistry in describing the *amounts* of initial reactant or final product gases which are consumed or produced in chemical reactions under a given set of conditions *before* the reaction takes place, or *after* it is finished. There are several ways to describe the amount of gas consumed or produced. The most direct way is to give the number of molecules (or moles) involved. Specifying the volume determines the amount of gas only indirectly since the volume of gas is

dependent on other variables, namely the temperature and pressure.

The **state** (Latin *status* - position) of a gas is determined by the values of the various measurements describing the physical condition of the gas. These measurable quantities will be referred to as *state variables*, since they each assume any set of continuous values, depending on the experimental conditions of the gas. The state variables relevant to gases are the number of mols (n), the *absolute* (Kelvin) temperature (**K**), the pressure (**P**), and the volume (**V**). An **equation of state** relates all the variables in one (mathematical) equation. Therefore, knowledge of the values of all the variables but one is sufficient to determine its value by solving the equation of state for the value of the unknown parameter. (See Section 3.4 on Solving Equations.)

Investigations into how gases behave during experiments led scientists to a number of useful relationships. These were thought to be universal in nature (apply to all gases under all conditions) and were called *Gas Laws*. Discovered over a period of 150 years (1666 - 1811), these “laws” (equations) were named after their discoverers.

In addressing a problem involving gases, it is necessary to be able to identify which law, or laws are applicable. To this end, we provide a graphical decision table algorithm for determining the appropriate laws to use. The *Gas Law Decision Table* categorizes various gas laws according to two parameters, number of substances, and number of conditions.¹ The questions one can ask about a single substance in a single state are absolute, in the sense that they are based on solving the Ideal Gas Law, presented in the next section, for one unknown. A single substance in two different states and two substances under the same conditions involve ratio laws presented in the following section. Two substances at two sets of conditions have too many variables to be relevant to simple situations.

The number and type of input variables are the key to deciding which law applies. The variables relevant to the laws in the table are given in braces. (p_i refers to partial pressure discussed in Section 15.5, and v_i refers to diffusion velocity.) Subscripts refer to a set of conditions or a component, as the case may be. In the case of chemical reactions, the gas laws may be used to determine the amount of substance before or after a reaction has taken place.

¹ Usually, no more than two substances are considered at one time.

Table 15.1 The Gas Law Decision Table

# Substances/ # States	One State	Two States
One Substance	Equation of State {P, V, n, T} <i>Ideal Gas Law</i>	Change of State {P ₁ , V ₁ , n ₁ , T ₁ } <i>Boyle, Charles, Avogadro, etc.</i>
Two Substances	Mixture {p _i , X _i } <i>Dalton</i> Diffusion {v _i , m _i } <i>Graham</i> Reaction {V _i , n _i } <i>Gay-Lussac</i>	(no examples)

15.3. The Ideal Gas Law

An equation of state which is capable of describing a given gas under rather general conditions can be quite complicated and difficult to solve. It may need to use *parameters* specific to the substance being described.² Fortunately, it follows from the nature of the gaseous

² A *parameter* is a quantity which is specific to a given object or situation. The parameters of a person's physical body would include weight, height, eye color, etc. Parameters might also be used to specify physical or psychological condition (health, mood, etc.). The distinction between parameters and variables can be subtle. A person in motion may be said to have a variable speed but constant weight, but in fact weight may be changing, particularly if speed of motion is dependent on conversion of matter into energy. In defining or describing a situation, such as an experiment or a model, those quantities which are assumed to remain constant (parameters) should be carefully stated and distinguished from those which are assumed to vary (variables)

phase (essentially isolated molecules) that under conditions of low pressure and/or high temperature, molecules behave independently and the equation of state becomes quite simple and general, and gases that may be so described are called *ideal*. That real gases behave nearly ideally under normal (ambient) conditions is why the simple equation of state was discovered by the early scientists.

Without ever seeing molecules, scientists in the 19th Century were able to deduce from experiments the essential features of gases on the molecular level. For example, based on the *model* that the information in sound waves is conveyed through molecular collisions, it is easy to deduce what the average speed of air molecules is equal to the velocity of sound in air (about 700 mi/hr). This (and every other prediction of the 19th Century) has been confirmed by direct observations in the 20th Century.

The central idea of the gaseous phase of matter is that molecules in motion are separated by enormous relative distances. The fundamental assumption of the basic model for gases, called the *Kinetic-Molecular Theory*, is that the average kinetic energy is directly proportional to the absolute (Kelvin) temperature.³ The mathematical expressions and physical laws of the behavior of gases which follow from this model are easy to derive from simple equations of motion.

Consider a cubical container filled with N gaseous molecules. The pressure P on a side of the container is given from physics as the force f per unit area, A . The total force, in turn, due to collisions on the wall by N molecules is given by Newton's Laws as N times the change in momentum (mass, m times velocity, v) divided by the time, t . Since the time it takes a molecule to travel the distance L between the walls of the container is L divided by the velocity, we have

$$f = PA = \frac{NMv}{t} = NM \frac{v^2}{L} \quad (15.1)$$

In the case of molecules in the gaseous phase, parameters of interest include molecular size and attractive force to other molecules. Variables are temperature, volume, pressure and amount.

³ This assumption is actually independent of the phase of the substance, and may be applied to liquids and solids as well. What distinguishes liquids and solids from gases is the distance between molecules. In the liquid and solid phases, the molecules are much closer than in the gas phase, causing the *intermolecular forces* to become important. Hence, the assumption that the distances are so great that the intermolecular forces can be ignored for gases.

Area times length of the container equals volume of the container, V . The basic assumption of the Kinetic-Molecular Theory is that kinetic energy, $\frac{1}{2}mv^2$ is proportional to T , or $mv^2 = kT$, so

$$PAL = PV = Nmv^2 = NkT \quad (15.2)$$

The number of moles of gas, n , is N/N_A , where N_A is Avogadro's number. The *molar gas constant*, R , is defined to be kN_A . Substituting for N gives the *Ideal Gas Law*:

$$PV = nN_A kT = nRT \quad (15.3)$$

It is only fair to point out that the notion of molecules in motion was not accepted by all the early atomists, including some greats like Dalton and Newton. Dalton believed that heat was not due to thermal motion, but to a substance (*caloric*) that the molecules could acquire, and he accepted Isaac Newton's derivation of Boyle's Law based on *potential* energy instead of *kinetic* energy.⁴ Energy is heat plus work, or kinetic energy plus potential energy. Disregarding any heat, the only contribution to the energy is the potential energy term, work, related to force moving through a distance:

$$E = PE = w = f \times d \quad (15.4)$$

In a gas, work is manifested macroscopically as the force of pressure across an area, sweeping out a volume:

$$w = f \times d = PA \times d = PV \quad (15.5)$$

Microscopically, work is manifested through forces of molecular attraction, which may be taken as inversely proportional to intermolecular distance (Section 4.4):

$$w = f \times d = \frac{\text{const}}{d} \times d = \text{const} \quad (15.6)$$

Thus, equating the macroscopic and microscopic expressions of work, $PV = \text{const}$.

The **Ideal Equation of State for gases**, or the **Ideal Gas Law** relates the volume (V), absolute temperature (T), pressure (P) and mols of gas (n) in terms of simple

⁴ Despite Newton's acceptance that heat was caused by motion of bodies, "putting their parts into a vibrating motion wherein heat consists" (*Opticks* by Sir Isaac Newton, Second English Edition, London, 1704, Query 5).

proportionalities:

$$PV = nRT \quad (15.7)$$

The pressure is usually measured in atmospheres or mm of mercury (in a barometer), called torr (1 atm \equiv 760 torr), after Torricelli, a Seventeenth Century Italian investigator of gases.⁵ Common metric units of volume are the cubic centimeter (cc), and the liter (1000 cc). Absolute temperature is measured in the fundamental SI unit Kelvin, K (named for the Nineteenth Century British physicist, William Thompson, who was titled Lord Kelvin). The Celsius⁶ (or centigrade) scale is defined relative to the Kelvin scale by

$$C = K - 273.15 \quad (15.8)$$

Don't forget to *always convert to K before using the ideal gas law*.

R is called the *molar gas constant*, and is an universal proportionality constant for all gases (which behave ideally). Its value depends on the units of the other variables in the equation. A value for R can be obtained from the observation that one mol of any gas under ideal conditions occupies 22.413837 L under one atmosphere pressure at 0 °C (273.15 K):

$$R = \frac{PV}{nT} = \frac{1 \text{ atm} \times 22.413837 \text{ L}}{1 \text{ mol} \times 273.15 \text{ K}} = 0.082056880 \text{ L} \cdot \text{atm/mol} \cdot \text{K} \quad (15.9)$$

15.4. Using the Ideal Gas Law

The ideal gas law is used two ways. The first uses it in an absolute sense to solve one equation (15.7) in one unknown. In this case, one should expect values for all the variable but one to be given in the statement of problem dealing with one substance in one state. This

⁵ Another was Galileo Galilei.

⁶ Named for Anders Celsius, an Eighteenth Century Swedish scientist.

form of the ideal gas law may be termed the *Equation of State Ideal Gas Law* equation.

Example 15.1 Determine the molar mass of 10 g of a gas which occupies a 1 L flask at 25 °C under 1.66 atm.

Recognizing that the number of mols n equals the mass m divided by the molar mass M :

$$PV = nRT = \frac{m}{M} RT$$

Therefore,

$$M = \frac{mRT}{PV} = \frac{10 \text{ g} \times 0.082057 \text{ L} \cdot \text{atm/mol} \cdot \text{K} \times 298.15 \text{ K}}{1.66 \text{ atm} \times 1 \text{ L}} = 147 \frac{\text{g}}{\text{mol}}$$

This value was used in Example 7.4 to determine the true molecular formula of $\text{C}_6\text{H}_4\text{Cl}_2$ and forms the basis of a method for determining molar masses of volatile substances attributed to Jean Baptiste Andre Dumas, 1826.

The other application of the ideal gas law is based on *changing conditions* of a gas. In this case the values of some variables are usually (but not always) held constant, and one is interested in how changes in some of the variables affect changes in others. In this case, the ideal gas equation is applied to two sets of conditions, called here *initial* and *final*, to produce two subscripted equations of the form Eq. (15.7), representing the gas at the two different conditions. Dividing one equation by the other and canceling the universal constant R yields the *Change of State Ideal Gas Law* equation:

$$\frac{P_f V_f}{n_f T_f} = \frac{P_i V_i}{n_i T_i} \quad (15.10)$$

A useful way to determine which type of ideal gas application is intended in a problem, is to enter the given information into a table. This also organizes one's thinking, and sets the problem up for simple solution with a calculator. Furthermore, if the author of the problem has forgotten to specify all the input information (as sometimes happens), this procedure will reveal what assumptions about the conditions are implicitly assumed, but not explicitly stated by the author.

The Ideal Gas Law Algorithm

Purpose: To determine the value of an unknown variable from the ideal gas equation.

Procedure:

1. Extract the numerical information from the statement of the question, converting temperatures to K if necessary. Organize the values (including units) into a table of the form given below. For each variable which is constant, simply enter its symbol.

	Initial Conditions	Final Conditions
P		
V		
n		
T		

- 2a. If none of the values of the variables (conditions) change, substitute the given values into the Equation of State Gas Law, Eqn. (15.7), (there will be three values in valid problems), together with the molar gas constant, and solve for the remaining unknown value.
- 2b. If any of the values of the variables change, substitute the entries from the table into the Change of State Ideal Gas Law, Eqn. (15.10), cancel constant quantities and solve for the value of the requested variable.

Example 15.2 A balloon which occupies 2.0 L at sea level where the temperature is 20.0 °C rises to an altitude where the temperature is 0.0 °C and the pressure is 200 torr. What is the volume of the balloon at the higher altitude?

In order to work this problem, one needs to know that the atmospheric pressure at sea level is defined to be one atmosphere, or 760 torr. Extracting the numerical information, converting it to the appropriate units, and organizing it into tabular form produces the following:

	Initial Conditions	Final Conditions
P	760 torr	200 torr
V	2.0 L	V_f
n	n	n
T	293.15 K	273.15 K

Note that the information in the problem may not be given in any particular order, but that the table organizes it for convenient computation. Because conditions are changing on a single gas (and not that the gas itself is changing due to chemical reaction), the *Change of State Gas Law*, Eq. (15.10) is indicated. Note that an implicit assumption has been made in the statement of the question that no gas escapes from the balloon ($n_f = n_i$). As you solve Eq. (15.10), note what the consequence of using 0.0 °C in the ideal gas equation would be.

Substituting the entries in the table into Eq. (15.10) produces:

$$\frac{(200 \text{ torr}) (V_f)}{(n) (273.15 \text{ K})} = \frac{(760 \text{ torr}) (2.0 \text{ L})}{(n) (293.15 \text{ K})}$$

Canceling n (which remains constant), and solving for the only unknown, V_f , yields 7.08 L (a reasonable value for a 2 L balloon expanding under an approximate four-fold reduction in pressure, and contracting slightly at slightly lower absolute temperature). Note that by including all the units in the equation, the correct units of the answer automatically appear.

15.5. Mixtures of Ideal Gases

In studying mixtures of two or more volatile (evaporatable) liquids, John Dalton discovered a simple relationship between the pressures of the individual components, referred to as *Dalton's Law of Partial Pressures*. It is an application of the Ideal Gas Law and may be derived from it as follows. Consider the Ideal Gas Law to apply to each component of a mixture of gases (a reasonable situation in the case of non-interacting molecules which behave independently of each other). At the same temperature and pressure, for each component i,

$$P_i = n_i \frac{RT}{V} \quad (15.11)$$

No subscripts are needed for T and V since they are fixed conditions for the mixture. Since gas molecules of the mixture behave independently, the ideal gas law must apply as well to the *total* pressure of the gas:

$$P_T = n_T \frac{RT}{V} \quad (15.12)$$

Dividing Eq. (15.11) by Eq. (15.12) gives

$$\frac{p_i}{P_T} = \frac{n_i}{n_T} = X_i \quad (15.13)$$

where X_i stands for the *molar fraction* of gas component i . Since the sum of the fractions of gas must add up to unity, Dalton's Law of Partial Pressures follows:

$$\sum X_i = 1 \Rightarrow \sum p_i = P_T \quad (15.14)$$

Dalton's Law of Partial Pressures has an important application in the calculation of the amount of a gas collected over water from a chemical reaction in the laboratory. When liquids evaporate, the gas produced is called *vapor*. The pressure of a vapor above the liquid is called the *vapor pressure*. The total pressure in a container which contains both a product gas and water vapor is the sum of the pressures of the two components by Dalton's law of partial pressures,

$$P_T = p_{\text{product gas}} + p_{\text{H}_2\text{O}} \quad (15.15)$$

The pressure of product gas is computed as the difference between the total pressure, P_T measured with a barometer, and the vapor pressure of water at the temperature of the experiment, listed in tables. Knowledge of the pressure, temperature and volume of gas collected permits a calculation of the number of mols of gas produced using the Equation of State Ideal Gas Law, Eq. 15.7.

Calculating the Amount of Gas Collected Over Water Algorithm

Purpose: To determine the amount of gas collected over water.

Procedure:

1. Determine the partial pressure of water, $p_{\text{H}_2\text{O}}$, at the temperature of the gas.
2. Calculate the pressure of the gas using Dalton's Law of Partial Pressures:

$$p_{\text{product gas}} = P_{\text{T}} - p_{\text{H}_2\text{O}}$$

3. Calculate the number of mols of gas produced using the Equation of State Ideal Gas Law:

$$n_{\text{product gas}} = \frac{p_{\text{product gas}} V}{RT}$$

Example 15.3 How many moles of O_2 are collected over water in a 500 mL vessel at 25 °C when the barometric pressure is 670.10 torr?

According to tables, the vapor pressure of water at 25 °C is 23.76 mm. (See also the calculation of the vapor pressure of water in Example 16.4.)

The pressure of O_2 is $(670.10 - 23.76) \text{ torr} = 646.34 \text{ torr} \times \left(\frac{1 \text{ atm}}{760 \text{ torr}}\right) = 0.85045 \text{ atm}$

The mols of O_2 collected is therefore

$$n_{\text{O}_2} = \frac{(0.85045 \text{ atm})(0.500 \text{ L})}{\left(0.082057 \frac{\text{L atm}}{\text{mol K}}\right)(298.25 \text{ K})} = 0.017381 \text{ mol O}_2$$

15.6. Gas Velocity

The kinetic molecular theory of gases is a mathematical model that describes the behavior of gases on the molecular level. One result which is easy to derive is an expression for the average speed of gas molecules. Collisions cause the speed of a given molecule to change, but the distribution of speeds for a large number of molecules is fixed, at a given

temperature. The Maxwell distribution of speed is related to the Boltzmann distribution of kinetic energy, eq. (10.11), through the relationship between velocity and kinetic energy, Eq. (4.7). A measure of average molecular speed can be easily derived from the equipartition theorem, Eq. (11.1), with $s = 3$ for three degrees of translational motion:

$$\overline{\text{KE}} = \frac{1}{2} \overline{mv^2} = \frac{3}{2} kT$$

where v is the molecular speed (velocity) and m is the molecular mass. Since the equipartition theorem applies to the *average* kinetic energy, the appropriate velocity to solve for is the square root of the velocity squared, or *root mean square (rms) velocity*. (The average of the absolute value of the velocity is a slightly different value.) Substituting the molar mass divided by Avogadro's number for the molecular mass, and the molar gas constant divided by Avogadro's number for Boltzmann's constant gives:

$$v_{\text{rms}} \equiv \sqrt{\overline{v^2}} = \sqrt{\frac{3RT}{M}} \quad (15.16)$$

Note that molecular speeds depend on only two parameters, molecular mass and absolute temperature.

Example 15.4 Calculate the rms speed of air molecules at 25 °C.

The atmosphere is 80% N_2 and 20% O_2 , with an average molar mass of 29. Noting that one Joule is defined as one kgm^2/s^2

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{(3)\left(\frac{8.3144\text{kg m}^2}{\text{mol K s}^2}\right)(298 \text{ K})}{\left(\frac{29\text{g}}{\text{mol}}\right)\left(\frac{1 \text{ kg}}{10^3 \text{ g}}\right)}} = 506 \frac{\text{m}}{\text{s}}$$

Thus we see that molecular speeds for typical molecules at room temperature are hundreds of meters per second. Since sound is carried by molecules, we can estimate the speed of sound in air:

$$506 \frac{\text{m}}{\text{s}} \left(\frac{3.2808 \text{ ft}}{1 \text{ m}}\right) = 1660 \frac{\text{ft}}{\text{s}} \left(\frac{1 \text{ mi}}{5280 \text{ m}}\right) \left(\frac{3600 \text{ s}}{1 \text{ hr}}\right) = 1132 \frac{\text{mi}}{\text{hr}}$$

Sound waves actually move slower than molecules, and the measured speed of sound in air at 25 °C is 346 m/s, or 774 mi/hr. Sonic booms are caused by objects going faster than sound (Mach 1).

Example 15.5 Estimate the frequency of molecular collisions in ambient air.

We have seen that average air molecules travel about 5×10^{14} pm/s. The density of air can be estimated from the molar volume of air at room temperature as an ideal gas (a good approximation):

$$\frac{22.414 \text{ L}}{1 \text{ mol}_{\text{STP}}} \left(\frac{273}{300}\right) \left(\frac{10^3 \text{ cm}^3}{1 \text{ L}}\right) \left(\frac{1^{10} \text{ pm}}{1 \text{ cm}}\right)^3 \left(\frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ molecules}}\right) = 3.39 \times 10^{10} \frac{\text{pm}^3}{\text{molecule}}$$

Equating the volume to that of a sphere containing the molecule and solving for the radius gives an estimate of the average distance separating molecules of 4.3×10^3 pm/molecule. Since the molecules are traveling about 5×10^{14} pm/s, a molecule will encounter about 10^{11} other molecules per second. Thus air molecules collide about 100 billion times per second. (More detailed calculations give about 10 billion collisions per second.)

15.7. Real Gases

The ideal gas model assumes negligible intermolecular interactions, which is realized at sufficiently low pressure and/or high temperature. Real gases have intermolecular attractions and repulsions. An improved equation of state for real gases constructed by J. van der Waals in 1873 corrects two terms in the ideal gas equation of state. Repulsions cause molecules to have finite size and reduce some of the available space of the container they occupy. Intermolecular attractions (discussed in Chapter 14) reduce the pressure of the gas. The form van der Waals chose to incorporate these corrections is

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \quad (15.17)$$

where the variables have the same meaning as for the ideal gas equation, and a and b are parameters characteristic of different gas substances. The reduction in volume due to

repulsions is obvious in the term in V . The reduction in pressure due to attractions is easier to see when the equation is solved for P . Many other mathematical gas state equations have been proposed over the years, but none completely matches experimental data over long ranges of temperature and pressure. The van der Waals equation is presented because it was the first attempt at a rational form, and it fits experimental data fairly well over reasonable ranges of variables.

The van der Waals equation is not as easy to work with as the ideal gas equation, because it is cubic in V . In fact, it is the equation that was used to illustrate numerical solution of equations (rather than algebraic solution), Example 3.6 of Chapter 3. Such calculations demonstrate how close to ideality real gases are.

The parameters a and b are determined by fitting the van der Waals equation to experimental gas state data. Typical values are given in Table 15.2.

Table 15.2 van der Waals Parameters

<i>Gas</i>	<i>a</i> (atm L ² /mol ²)	<i>b</i> (L/mol)
<i>Atoms</i>		
He	0.03412	0.02370
Ne	0.2107	0.01709
Ar	1.345	0.03219
Kr	2.318	0.03987
Xe	4.194	0.05105
<i>Non-polar Molecules</i>		
H ₂	0.2444	0.02661
O ₂	1.360	0.03183
N ₂	1.390	0.03913
CH ₄	2.253	0.04278
CO ₂	3.592	0.04267
O ₃	3.545	0.04903
Cl ₂	6.493	0.05622
<i>Polar Molecules</i>		
HCl	3.667	0.04081
HBr	4.451	0.04431
H ₂ O	5.464	0.03049
H ₂ S	4.431	0.04287
SO ₂	6.714	0.05636
CH ₃ OH	9.523	0.06702

Since the nb term represents excluded volume, the parameter b should be directly related to the volume of one mol of molecules. The parameter a has an interpretation in terms of the binding energy of the molecules. The trends in size and intermolecular attractions reflected by the magnitudes of a and b are apparent. Although water and methyl alcohol have hydrogen bonding, sulfur dioxide has greater dispersion forces due to a greater number of

electrons (see Section 10.2).

Example 15.6 Estimate the radius of a neon atom from van der Waals parameters.

The parameter b represents the volume excluded by a pair of touching spherical atoms whose centers are 2 atomic radii apart. Convert the units of b from Table 15.2 into molecular-sized units, equate it to one-half the volume of a sphere of radius $2r$ (since two spheres are excluded), and solve for the atomic radius r .

$$\begin{aligned} b_{\text{Ne}} &= 0.01709 \frac{\text{L}}{\text{mol}} \left(\frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ molecules}} \right) \times \left(\frac{10^3 \text{ mL}}{1 \text{ L}} \right) \times \left(\frac{10^{10} \text{ pm}}{1 \text{ cm}} \right)^3 \\ &= 2.854 \times 10^7 \frac{\text{pm}^3}{\text{molecule}} = \frac{1}{2} \left[\frac{4}{3} \pi (2r)^3 \right] \\ r_{\text{Ne}} &= 119 \text{ pm} \end{aligned}$$

The van der Waals radii determined from gases may be compared with those determined from densities of solids (cf. Example 15.4). Various methods for determining atomic radii from experiments may not agree. There are a number of reasons for this. The van der Waals equation is based on a mathematical *model* of gases, and doesn't have to match reality (other non-ideal gas equations of state give different values for radii). Also, molecules can't be of fixed size anyway, because according to wave mechanics the electrons are not particles, but can be thought of as a cloud of charge density distributed non-uniformly over space, so assigning sizes is ambiguous (see Section 7.5 on the wave mechanics of atoms). The wave-mechanical atomic size may be estimated from the interatomic distance at minimum potential interaction. Table 12.1 shows this to be 310 nm, considerably larger than the radius measured for colliding neon atoms in the gas phase. Nevertheless, it is remarkable that Nineteenth Century scientists could obtain reasonable estimates of the sizes of such tiny objects as atoms and molecules long before they could be magnified into visibility and "seen" directly.

Summary

The gas phase results from large separation of molecules. Independent motion simplifies the description of the states of gases.

Quantitative statements result from solving the equation of state for one unknown. The Gas Law Decision Table and Change of State Ideal Gas Law Algorithm help organize data

into meaningful statements in the form of equations which may be solved using algebraic manipulations. In the case of gases collision models yield equations describing the behavior in terms of the state variables pressure, volume, amount and temperature. Ideal gases assume zero interaction forces, leading to the ideal gas equation of state. Non-ideal equations of state take interactions into account.

GAS STATE EXERCISES

1. What's wrong with the question, "what is the volume of gas at room temperature?"?
2. By what factor would the temperature have to fall at an altitude where the pressure on a balloon decreased by a factor of two but the volume did not change?
3. What is the change in pressure in a pressure cooker?
4. Derive *Dalton's Law of Partial Volumes*: the *volume* of a mixture of gases is additive at constant *pressure*.
5. Derive *Graham's Law of Diffusion*: the relative rate of gaseous diffusion is inversely proportional to the square root of the mass.
6. Find the van der Waals radius of a chlorine atom.

GAS STATE EXERCISE HINTS

1. Consider the meaning of the state of a substance.
2. Assume no gas escapes from the balloon.
3. A pressure cooker may be assumed to be a closed container containing boiling water.
4. Follow the same steps as for Dalton's Law of Partial Pressures at constant pressure.
5. According to the Kinetic-Molecular Theory, $K. E. = 1/2 mv^2 = kT$.
6. Don't forget that elemental chlorine is diatomic.