

Properties of Gases

a Chem1 Supplement Text

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Throughout much of human history, “airs” or gases were not believed to be *matter* at all; their apparently weightless nature and their ability to move about freely and fill all available space, while carrying with them definite physical properties such as odor and sometimes color, conferred upon them a somewhat mysterious nature. Even the scientist Robert Boyle wrote about “*The Strange Subtlety, Great Efficacy and Determinate Nature of Effluviiums*”.

The invention of the sensitive balance in the early seventeenth century showed once and for all that gases are matter, and the “pneumatic era” of chemistry was thus launched; the behavior of gases was soon to prove an invaluable tool in the development of the atomic theory of matter.

We begin our formal study of matter in this course with the study of gases because here we can see the behavior of matter at its simplest: individual molecules, acting as individuals, almost completely uncomplicated by interactions and interferences between each other. Later on, our knowledge of gases will serve as the pathway to our understanding of the far more complicated *condensed phases* (liquids and solids); here, the theory of gases will no longer give us correct answers, but it will provide us with a *model* that will at least help us to rationalize the behavior of these more complicated states of matter.

1 Observable properties of gases

Let us start with what we can observe experimentally about gases. First, we know that a gas has no definite volume or shape; a gas will fill whatever volume is available to it. This property of *diffusion* implies that the molecular units of a gas are in rapid, random motion, and that they are far enough away from each other that this motion is unimpeded by interactions between the molecules.

The other outstanding characteristic of gases, their low *densities*, is another indication that the average distance between molecules is very large. One mole of H₂O molecules at 100 °C at 1 atm pressure occupies a volume of 18.8 cm³, whereas the same quantity of water vapor at the same temperature and pressure has a volume of 30200 cm³, more than 1000 times greater.

The most remarkable property of gases, however, is that to a very good approximation, they all behave the same way in response to changes in temperature and pressure, expanding or contracting by predictable amounts. This is very different from the behavior of liquids or solids, in which the properties of each particular substance must be determined individually.

Pressure exerted by a gas

Pressure is defined as force per unit area. To visualize this, imagine some gas trapped in a cylinder having one end enclosed by a freely moving piston. In order to keep the gas in the container, a certain amount of weight (force, f) must be placed on the piston so as to exactly balance the force exerted by the gas on the bottom of the piston, and tending to push it up. The pressure of the gas is simply the quotient f/A , where A is the cross-section area of the piston.

The barometer The column of air above us exerts a force on each 1-cm² of surface equivalent to a weight of about 1034 g¹. In the early 17th century the Italian Evangelista Torricelli invented a device to measure this pressure. The *barometer* consists of a vertical glass tube closed at the top and evacuated, and open at the bottom, where it is immersed in a dish of a liquid. The atmospheric pressure acting on this liquid will force it up into the evacuated tube until the weight of the liquid column exactly balances the atmospheric pressure. If the liquid is mercury, the height supported will be about 760 cm; this height corresponds to *standard atmospheric pressure*.

¹This figure is obtained by solving Newton's law $f = ma$ for m , using the acceleration of gravity for a :

$$m = \frac{f}{a} = \frac{101375 \text{ kg m}^{-1} \text{ s}^{-2}}{9.8 \text{ m s}^{-2}} = 10340 \text{ kg m}^{-2} \text{ s}^{-1} = 1034 \text{ g cm}^{-2}$$

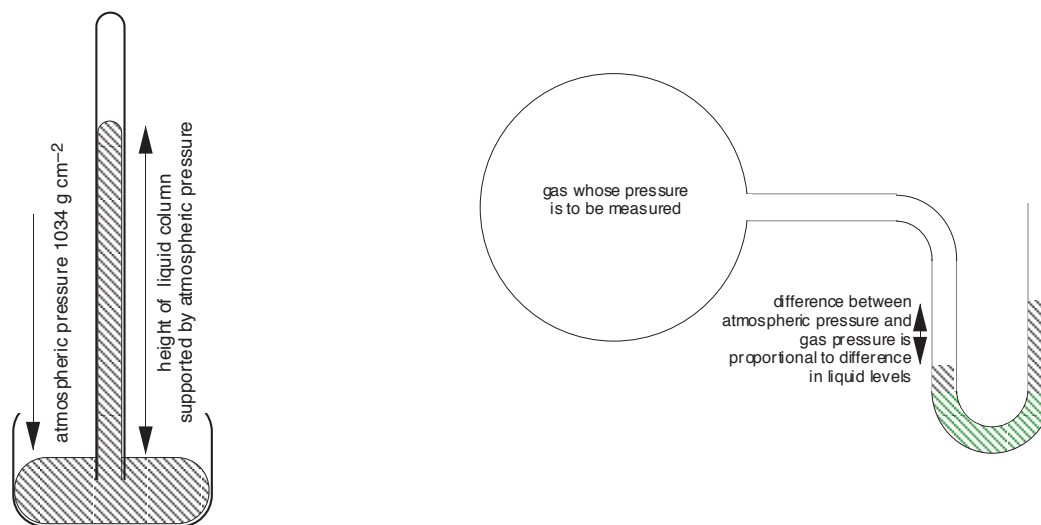


Figure 1: Measurement of gas pressure: the barometer and manometer

A modification of the barometer, the *U-tube manometer*, provides a simple device for measuring the pressure of any gas in a container. The U-tube is partially filled with mercury, one end is connected to container, while the other end is left open to the atmosphere. The pressure inside the container is found from the difference in height between the mercury in the two sides of the U-tube.

Pressure units The unit of pressure in the SI system is the *pascal* (Pa), defined as a force of one newton per square metre (Nm^{-2} or $\text{kg m}^{-1}\text{s}^{-2}$). In chemistry, it is more common to express pressures in units of *atmospheres* or *torr*:

$$1 \text{ atm} = 1.01325\text{E}5 \text{ Pa} = 760 \text{ torr}$$

The older unit *millimetre of mercury* (mm Hg) is almost the same as the torr; it is defined as one mm of level difference in a mercury barometer at 0°C . In meteorology, the pressure unit most commonly used is the *bar*; $1 \text{ bar} = 10^5 \text{ N m}^{-2} = 0.987 \text{ atm}$. In engineering work the *pound per square inch* is often used; standard atmospheric pressure is 14.7 psi.

The volume occupied by a gas

The *volume* of a gas is simply the space in which the molecules of the gas are free to move. If we have a mixture of gases, such as air, the various gases will occupy

the same volume at the same time, since they can all move about freely. The volume of a gas can be measured by trapping it above mercury in a calibrated tube known as a *gas burette*. The SI unit of volume is the cubic metre, but in chemistry we more commonly use the *litre* and the *millilitre* (ml). The *cubic centimetre* (cc) is also frequently used; it is very close to 1 ml.

The temperature of a gas

If two bodies are at different temperatures, heat will flow from the warmer to the cooler one until their temperatures are the same. This is the principle on which *thermometry* is based; the temperature of an object is measured indirectly by placing a calibrated device known as a *thermometer* in contact with it. When thermal equilibrium is obtained, the temperature of the thermometer is the same as the temperature of the object.

Temperature scales

A thermometer makes use of some temperature-dependent quantity, such as the density of a liquid, to allow the temperature to be found indirectly through some easily measured quantity such as the length of a mercury column. The resulting scale of temperature is entirely arbitrary; it is defined by locating its zero point, and the size of the *degree* unit.

The Celsius temperature scale locates the zero point at the freezing temperature of water; the Celsius degree is defined as 1/100 of the difference between the freezing and boiling temperatures of water at 1 atm pressure.

The older *Fahrenheit* scale placed the zero point at what was imagined to be the coldest possible temperature in England at the time, and the 100° point coincided approximately with body temperature. On this scale, water freezes at 32°F and boils at 212°F. The Fahrenheit scale is a finer one than the Celsius scale; there are 180 Fahrenheit degrees in the same temperature interval that contains 100 Celsius degrees, so $1\text{C}^\circ = \frac{9}{5}\text{F}^\circ$. Since the zero points are also different by 32F°, conversion between temperatures expressed on the two scales requires the addition or subtraction of this offset, as well as multiplication by the ratio of the degree size².

Absolute temperature

In 1787 the French mathematician and physicist Jacques Charles discovered that for each Celsius degree that the temperature of a gas is lowered, the volume of

²You should be able to derive the formula for this conversion. Notice also that temperature is expressed by placing the degree symbol in front of the scale abbreviation (37°C), whereas a temperature *interval* is written with the degree sign *following* the symbol (3C°).

the gas will diminish by $\frac{1}{273}$ of its volume at 0°C . The obvious implication of this is that if the temperature could be reduced to -273°C , the volume of the gas would contract to zero. Of course, all real gases condense to liquids before this happens, but at sufficiently low pressures their volumes are linear functions of the temperature (*Charles' Law*), and extrapolation of a plot of volume as a function of temperature predicts zero volume at -273.15°C (See Fig. 3). This temperature, known as *absolute zero*, corresponds to the total absence of thermal energy.

The temperature scale on which the zero point is -273.15°C was suggested by Lord Kelvin, and is usually known as the *Kelvin* scale. Since the size of the Kelvin and Celsius degrees are the same, conversion between the two scales is a simple matter of adding or subtracting 273.15; thus room temperature, 20°C , is about 293°K . Because the Kelvin scale is based on an absolute, rather than on an arbitrary zero of temperature, it plays a special significance in scientific calculations; most fundamental physical relations involving temperature are expressed mathematically in terms of absolute temperature. In engineering work, an absolute scale based on the Fahrenheit degree is commonly used; this is known as the Rankine scale.

2 Empirical laws of gas behavior

Pressure-volume: Boyle's Law

Robert Boyle³ showed that the volume of air trapped by a liquid in the closed short limb of a J-shaped tube decreased in exact proportion to the pressure produced by the liquid in the long part of the tube. The trapped air acted much like a spring, exerting a force opposing its compression. Boyle called this effect "the spring of the air", and published his results in a pamphlet of that title.

Boyle's law can be expressed as

$$PV = \text{constant} \tag{1}$$

and is true only if the number of molecules n and the temperature are held constant. This is an equation of *inverse proportionality*; any change in the pressure is exactly compensated by an opposing change in the volume. As the pressure decreases toward zero, the volume will increase without limit. Conversely, as the pressure is increased, the volume decreases, but can never reach zero. A plot of the pressure of an ideal gas as a function of its volume yields a plot

³Robert Boyle (1627-1691) was an English natural philosopher and early believer in atomism whose inquiring mind and prolific writings have led many to call him the father of chemistry. His famous book *The Skeptical Chymist*, the first Chemistry book ever written, laid the foundations for the further development of atomic theory.

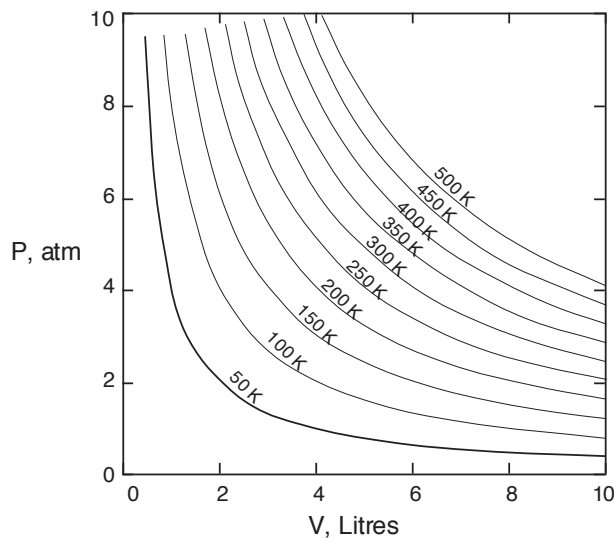


Figure 2: Boyle's law: pressure-volume isotherms of an ideal gas

whose form is that of a *hyperbola*. There will be a separate P - V plot for each temperature; a single P - V plot is therefore called an *isotherm*.

A related type of plot with which you should be familiar shows the product PV as a function of P . You should understand why this yields a straight line, and how the position of this line varies with the temperature.

Volume and temperature: Charles' law

The discovery that all gases expand by the same amount as the temperature is raised was made independently by the French scientists Jacques Charles (1746-1823) and Joseph Gay-Lussac (1778-1850). This relation is now usually stated more explicitly: *the volume of a gas confined against a constant pressure is directly proportional to the absolute temperature.*

Volume and number of molecules: Avogadro's law

Gay-Lussac noticed that when two gases react, they do so in volume ratios that can always be expressed as small whole numbers. Thus when hydrogen burns in oxygen, the volume of hydrogen consumed is always exactly twice the volume of oxygen. The Italian scientist Amadeo Avogadro drew the crucial conclusion: these volume ratios must be related to the relative numbers of molecules that react, and so *equal volumes of gases, measured at the same temperature and pressure, contain equal numbers of molecules.* Avogadro's law thus predicts a

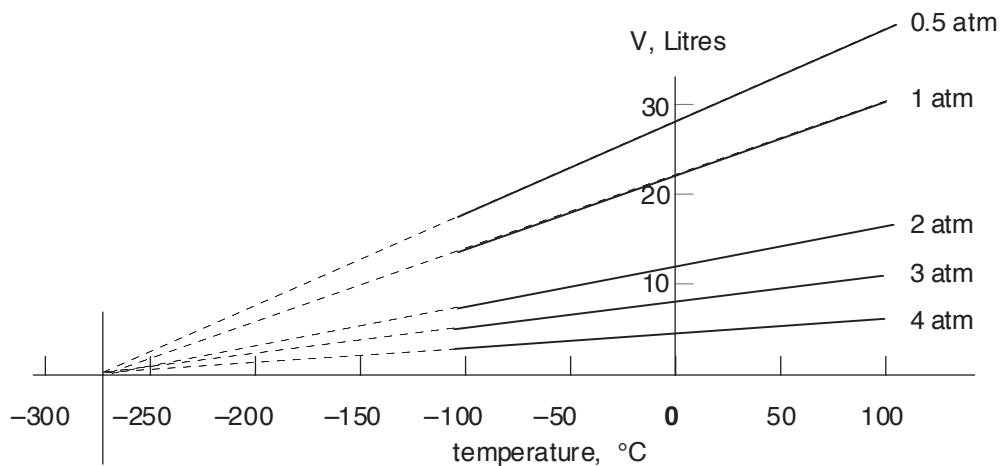


Figure 3: The law of Charles and Gay-Lussac: temperature dependence of the volume

directly proportional relation between the number of moles of a gas and its volume.

The ideal gas equation of state

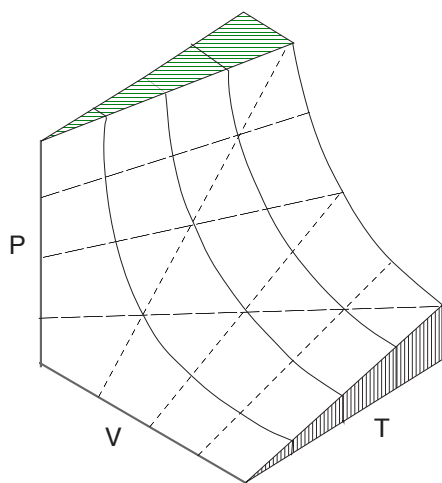
If the variables n , P , V , and T have known values, then a gas is said to be in a definite *state*, meaning that all other physical properties of the gas are also defined. The relation between these state variables is known as an *equation of state*.

The ideal gas equation of state can be derived by combining the expressions of Boyle's, Charles', and Avogadro's laws (you should be able to do this!). This equation is usually written

$$PV = nRT \quad (2)$$

where the proportionality constant R is known as the *gas constant*. This is one of the few equations you must commit to memory in this course; you should also know the common value and units of R .

An *ideal gas* is defined as a hypothetical substance that obeys the ideal gas equation of state. We will see later that all real gases behave more and more like an ideal gas as the pressure approaches zero. A pressure of only 1 atm is sufficiently close to zero to make this relation useful for most gases at this pressure.



Each point on this surface represents a possible combination of (P, V, T) for an ideal gas. The three sets of lines inscribed on the surface correspond to states in which one of these three variables is held constant. The curved lines, being lines of constant temperature, are *isotherms*, and are plots of Boyle's law. The long-dashed lines are *isobars* and represent Charles' law plots. The short-dashed lines, known as *isochors*, show all values of (P, T) consistent with various fixed *volumes*.

Figure 4: P - V - T behavior of an ideal gas

Molar volume of a gas: standard temperature and pressure

The set of conditions $T = 273\text{K}$ and $P = 1\text{atm}$ is known as *standard temperature and pressure*, usually denoted STP. Substituting these values into the ideal gas equation of state and solving for V yields a volume of 22.414 litres for 1 mole.

The standard molar volume 22.4 L mol^{-1} is a value worth memorizing, but remember also that it is valid only at STP. The molar volume at other temperatures and pressures can easily be found by simple proportion.

Problem Example 1

Calculate the approximate molar mass of a gas whose measured density is 3.33 g/L at 30°C and 780 torr .

Solution. From the ideal gas equation, the number of moles contained in one litre of the gas is

$$n = \frac{PV}{RT} = \frac{780/760\text{ atm}(1.00\text{ L})}{(.08201\text{ L atm mol}^{-1}\text{ K})(393\text{K})} = .0413\text{ mol}$$

The molecular weight is therefore

$$(3.33\text{ g L}^{-1})/(0.0413\text{ mol L}^{-1}) = 80.6\text{ g mol}^{-1}$$

Problem Example 2

Estimate the average distance between the molecules in a gas at 1 atm pressure and 0°C .

Solution. Consider a 1-cm^3 volume of the gas, which will contain $6.02\text{E}23/22400 = 2.69\text{E}19$ molecules. The volume per molecule (not the same as the volume of a molecule, which for an ideal gas is zero!) is just the reciprocal of this, or $3.72 \times 10^{-20}\text{ cm}^3$. Assume that the molecules are evenly distributed so that each occupies an imaginary box having this volume. The average distance between the centers of the molecules will be defined by the length of this box, which is the cube root of the volume per molecule:

$$(3.72 \times 10^{-20})^{\frac{1}{3}} = 3.38 \times 10^{-7}\text{ cm} = 3.4\text{ nm}$$

Molecular weight and density of a gas

Since all gases have the same molar volume at the same temperature and pressure, we can easily determine the number of moles contained in a sample of any

gas. If, in addition, we measure the *mass* of the gas, we can determine its molar mass.

This is the basis of a simple and widely used procedure for determining the molecular weight of a substance. It is known as the *Dumas method*, after the French chemist Jean Dumas (1800-1840) who developed it. One simply measures the weight of a known volume of gas and converts this volume to its STP equivalent, using Boyle's and Charles' laws. The weight of the gas divided by its STP volume yields the density of the gas, and the density multiplied by 22.4 L mol^{-1} gives the molecular weight.

Pay careful attention to the examples of gas density calculations shown in your textbook. You will be expected to carry out calculations of this kind, converting between molecular weight and gas density (mass and volume).

Problem Example 3

A mixture of O_2 and nitrous oxide, N_2O is sometimes used as a mild anesthetic in dental surgery. A certain mixture of these gases has a density of 1.482 g L^{-1} at 25°C and 0.980 atm . What was the mole-percent of N_2O in this mixture?

Solution: First, find the density the gas would have at STP:

$$(1.482 \text{ g L}^{-1}) \times \left(\frac{298}{273}\right) \left(\frac{1}{.980}\right) = 1.65 \text{ g L}^{-1}$$

The molar mass of the mixture is $(5 \text{ g L}^{-1})(22.4 \text{ L mol}^{-1}) = 37.0 \text{ g mol}^{-1}$. The molecular weights of O_2 and N_2O are 32 and 44, respectively. Thus the fraction of the heavier gas in the mixture is

$$\frac{37 - 32}{44 - 32} = \frac{5}{12} = .42$$

3 Mixtures of gases: Dalton's law of partial pressures

The ideal gas equation of state applies to mixtures just as to pure gases. It was in fact with a gas mixture, ordinary air, that Boyle, Gay-Lussac and Charles did their early experiments. The only new concept we need in order to deal with gas mixtures is the *partial pressure*.

The pressure exerted by a gas depends on the force exerted by each molecular collision with the walls of the container, and on the number of such collisions in a unit of area per unit time. If a gas contains two kinds of molecules, each species will engage in such collisions, and thus make a contribution to the total

pressure in exact proportion to its abundance in the mixture. The contribution that each species makes to the total pressure of the gas is known as the *partial pressure* of that species.

The above is essentially a statement of *Dalton's law of partmal pressures*. Algebraically, we can express this law by

$$P_{\text{total}} = P_1 + P_2 + \dots = \sum_i P_i \quad (3)$$

Dalton himself stated this law in a simple and vivid way:

Every gas is a vacuum to every other gas.

The partial pressure of any one gas is directly proportional to its abundance in the mixture, and is just the total pressure multiplied by the *mole fraction* of that gas in the mixture⁴.

For example, about 78% of the molecules of air consist of nitrogen. The mole fraction of N₂ in air is therefore 0.78, and the partial pressure of N₂ in air is 0.78 times the atmospheric pressure.

Molar mass of a gas mixture A gas made up of more than one kind of molecule will have a molar mass that is a weighted average of the molar masses of its components. (By the way, the older term “molecular weight” implies a certain mass possessed by individual molecules, so it is commonly modified by the prefix “average” in the context of a gas mixture.)

The molar mass of a mixture of gases is just the sum of the mole fraction of each gas, multiplied by the molar mass of that substance. The molar mass of dry air, for example, is approximately

$$(0.78 \times 28 \text{ g mol}^{-1}) + (0.21 \times 32 \text{ g mol}^{-1}) = 28.6 \text{ g mol}^{-1}$$

4 The kinetic molecular theory of gases

The properties such as temperature, pressure, and volume, together with other properties related to them (density, thermal conductivity, etc.) are known as *macroscopic* properties of matter; these are properties that can be observed in bulk matter, without reference to its underlying structure or molecular nature.

By the late 19th century the atomic theory of matter was sufficiently well accepted that scientists began to relate these macroscopic properties to the

⁴The mole fraction is just the number of moles of a given substance, divided by the number of moles of all substances present in the mixture; thus for substance i , $X_i = n_i \div \sum_j n_j$.

behavior of the individual molecules, which are described by the *microscopic* properties of matter. The outcome of this effort was the *kinetic molecular theory* of gases. This theory applies strictly only to a hypothetical substance known as an *ideal gas*; we will see, however, that it describes the behavior of real gases at ordinary temperatures and pressures quite accurately, and serves as an extremely useful model for treating gases under non-ideal conditions as well.

The basic tenets of the kinetic-molecular theory are as follows:

1. A gas is composed of molecules that are separated by average distances that are much greater than the sizes of the molecules themselves. *The volume occupied by the molecules of the gas is negligible compared to the volume of the gas itself.*
2. The molecules of an ideal gas exert no attractive forces on each other, or on the walls of the container.
3. The molecules are in constant random motion, and as material bodies, they obey Newton's laws of motion. This means that the molecules move in straight lines until they collide with each other or with the walls of the container.
4. Collisions are perfectly *elastic*; when two molecules collide, they change their directions and kinetic energies, but the total kinetic energy is conserved. *Collisions are not "sticky".*
5. The average kinetic energy of the gas molecules is directly proportional to the absolute temperature. (Notice that the term "average" is very important here; the velocities and kinetic energies of individual molecules will span a wide range of values, and some will even have zero velocity at a given instant.) This implies that all molecular motion would cease if the temperature were reduced to absolute zero.

According to this model, most of the volume occupied by a gas is empty space; this is the main feature that distinguishes gases from other forms of matter, in which the molecules are constantly in contact with each other. The gas molecules are in rapid and continuous motion; at ordinary temperatures and pressures their velocities are of the order of 0.1-1 km/sec and each molecule experiences approximately 10^{10} collisions with other molecules every second.

Kinetic interpretation of gas pressure The kinetic molecular theory makes it easy to see why a gas should exert a pressure on the walls of a container. Any surface in contact with the gas is constantly bombarded by the molecules. At each collision, a molecule moving with momentum mv strikes the surface. Since the collisions are elastic, the molecule bounces back with the same velocity in

the opposite direction. This change in velocity Δv in a time interval Δt is equivalent to an acceleration; from Newton's second law $F = ma$, a force F is thus exerted on the surface of area A , exerting a pressure F/A .

Kinetic interpretation of temperature According to the kinetic molecular theory, the average kinetic energy of an ideal gas is directly proportional to the temperature. Kinetic energy is the energy a body has by virtue of its motion:

$$\text{ke} = \frac{mv^2}{2}$$

As the temperature of a gas rises, the average velocity of the molecules will increase; a doubling of the temperature will increase this velocity by a factor of four. Collisions with the walls of the container will transfer more momentum, and thus more kinetic energy, to the walls. If the walls are cooler than the gas, they will get warmer, returning less kinetic energy to the gas, and causing it to cool until thermal equilibrium is reached.

Because temperature depends on the *average* kinetic energy, the concept of temperature only applies to a statistically meaningful sample of molecules. We will have more to say about molecular velocities and kinetic energies farther on.

Kinetic explanation of Boyle's law Boyle's law is easily explained by the kinetic molecular theory. The pressure of a gas depends on the number of times per second that the molecules strike the surface of the container. If we compress the gas to a smaller volume, the same number of molecules are now acting against a smaller surface area, so the number striking per unit of area, and thus the pressure, is now greater.

Kinetic explanation of Charles' law Kinetic molecular theory states that an increase in temperature raises the average kinetic energy of the molecules. If the molecules are moving more rapidly but the pressure remains the same, then the molecules must stay farther apart, so that the increase in the rate at which molecules collide with the surface of the container is compensated for by a corresponding increase in the area of this surface as the gas expands.

Kinetic explanation of Avogadro's law If we increase the number of gas molecules in a closed container, more of them will collide with the walls per unit time. If the pressure is to remain constant, the volume must increase in proportion, so that the molecules strike the walls less frequently, and over a larger surface area.

Kinetic interpretation of gas viscosity

The molecular motion due to the temperature is sometimes called *thermal* motion; it is always present, and is of course entirely random in nature. If the gas is flowing through a pipe or tube, then an additional non-random translational motion is superimposed on the thermal motion, and this is what we think of as the “flow” of the gas.

There is a slight problem, however. Molecules flowing near the center of the pipe collide mostly with molecules moving in the same direction at about the same velocity, but those that happen to find themselves near the wall will experience frequent collisions with the wall. Since the molecules in the wall of the pipe are not moving in the direction of the flow, they will tend to absorb more kinetic energy than they return, with the result that the gas molecules closest to the wall of the pipe are slowed down. Their random thermal motion will eventually take them deeper into the stream, where they will collide with other flowing molecules and slow them down. This gives rise to a resistance to flow known as *viscosity*, and is the reason why a large number of pumping stations are needed to force gas to flow through a long pipeline such as the one extending from Calgary to Vancouver.

Effusion, diffusion and Graham’s law

If a tiny hole is made in the wall of a vessel containing a gas, then the rate at which gas molecules leak out of the container will be proportional to the number of molecules that collide with unit area of the wall per second, and thus with the rms-average velocity of the gas molecules. This process, when carried out under idealized conditions, is known as *effusion*.

Around 1830, the English chemist Thomas Graham (1805-1869) discovered that the relative rates at which two different gases, at the same temperature and pressure, will effuse through identical openings is inversely proportional to the square root of its molar mass.

$$v_{\text{effusion}} \propto \frac{1}{\sqrt{M}} \quad (4)$$

Graham’s law, as this relation is known, is a simple consequence of the square-root relation between the velocity of a body and its kinetic energy.

According to the kinetic molecular theory, the molecules of two gases at the same temperature will possess the same average kinetic energy. If \bar{v}_1 and \bar{v}_2 are the average velocities of the two kinds of molecules, then at any given temperature $ke_1 = ke_2$ and

$$\frac{1}{2}m_1\bar{v}_1^2 = \frac{1}{2}m_2\bar{v}_2^2 \quad (5)$$

or, in terms of molar masses M ,

$$\frac{\bar{v}_1}{\bar{v}_2} = \sqrt{\frac{M_2}{M_1}} \quad (6)$$

Thus the average velocity of the lighter molecules must be greater than those of the heavier molecules, and the ratio of these velocities will be given by the inverse ratio of square roots of the molecular weights.

Although the conditions under which Graham's law applies exactly are very restrictive⁵, the law provides insight into a wide range of phenomena that depend on the relative average velocities of molecules of different masses.

One application of this principle that was originally suggested by Graham himself but was not realized on a practical basis until a century later is the separation of isotopes. The most important example is the enrichment of uranium in the production of nuclear fission fuel. Uranium consists mostly of U^{238} , with only 0.7% of the fissionable isotope U^{235} . Uranium is of course a metal, but it reacts with fluorine to form a gaseous hexafluoride, UF_6 . In the very successful *gaseous diffusion process* the UF_6 diffuses repeatedly through a porous wall. Each time, the lighter isotope passes through a bit more rapidly than the heavier one, yielding a mixture that is minutely richer in U^{235} . The process must be repeated thousands of times to achieve the desired degree of enrichment.

5 More on the kinetic theory of gases

One reason the ideal gas is considered so important is that it is the only state of matter whose properties can be precisely calculated from simple mechanics. Even though they yield correct answers only for ideal gases, these calculations (and the ideas on which they are based) can serve as very useful models to help us understand the behavior of real gases, and to a limited extent, liquids as well. Your emphasis in this section should be on understanding these models and the ideas behind them, rather than in memorizing the various equations.

The velocities of gas molecules

The trajectory of an individual gas molecule consists of a series of straight-line paths interrupted by collisions. What happens when two molecules collide depends on their relative kinetic energies; in general, a faster or heavier molecule

⁵Graham's law is valid only under very restrictive conditions, the most important one being that no other gases are present. Contrary to what is written in some textbooks and is often taught, Graham's Law does *not* accurately predict the relative rates of escape of the different components of a gaseous mixture into the outside air, nor does it give the rates at which two gases will diffuse through another gas such as air. See "Misuse of Graham's Laws" by Stephen J. Hawkes, *J. Chem. Education* **70**(10) 836-837 1993.

will impart some of its kinetic energy to a slower or lighter one. Two molecules having identical masses and moving in opposite directions at the same speed will momentarily remain motionless after their collision.

If we could measure the instantaneous velocities of all the molecules in a sample of a gas at some fixed temperature, we would obtain a wide range of values. A few would be zero, and a few would be very high velocities, but the majority would fall into a more or less well defined range. We might be tempted to define an average velocity for a collection of molecules, but here we would need to be careful: molecules moving in opposite directions have velocities of opposite signs. Because the molecules are in a gas are in random thermal motion, there will be just about as many molecules moving in one direction as in the opposite direction, so the velocity vectors of opposite signs would all cancel and the average velocity would come out to zero. Since this answer is not very useful, we need to do our averaging in a slightly different way.

The proper treatment is to average the *squares* of the velocities, and then take the square root of this value. The resulting quantity is known as the *root mean square*, or *RMS* velocity

$$v_{\text{rms}} \equiv \sqrt{\frac{\sum v^2}{n}} \quad (7)$$

which we will denote simply by \bar{v} .

The formula relating the RMS velocity to the temperature and molar mass is surprisingly simple, considering the great complexity of the events it represents:

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}} \quad (8)$$

in which $k = R \div 6.02E23$, the “gas constant per molecule”, is known as the *Boltzmann constant*.

Problem Example 4

What is v_{rms} of a nitrogen molecule at 300K?

Solution. The molar mass of N_2 is 28.01. Substituting in Eq 8 and expressing R in energy units, we obtain

$$\tilde{v}^2 = \frac{3 \times 8.31 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{28.01 \times 10^{-3} \text{ kg mol}^{-1}}$$

which works out to $2.67E5 \text{ J kg}^{-1}$. Recalling the definition of the joule, $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$ and taking the square root,

$$v_{\text{rms}} = \sqrt{2.67E5 \text{ J kg}^{-1} \times \frac{1 \text{ kg m}^2 \text{ s}^{-2}}{1 \text{ J}}} = 517 \text{ m s}^{-1}$$

or

$$517 \text{ m s}^{-1} \times \frac{1 \text{ km}}{10^3 \text{ m}} \times \frac{3600 \text{ s}}{1 \text{ h}} = 1860 \text{ km h}^{-1}$$

The Boltzmann distribution

If we were to plot the number of molecules whose velocities fall within a series of narrow ranges, we would obtain a slightly asymmetric curve known as a *velocity distribution*. The peak of this curve would correspond to the *most probable* velocity. This velocity distribution curve is known as the *Maxwell-Boltzmann distribution*⁶.

The derivation of the Boltzmann curve is a bit too complicated to go into here, but its physical basis is easy to understand. Consider a large population of molecules having some fixed amount of kinetic energy. As long as the temperature remains constant, this total energy will remain unchanged, but it can be distributed among the molecules in many different ways, and this distribution will change continually as the molecules collide with each other and with the walls of the container.

It turns out, however, that kinetic energy is acquired and handed around only in discrete amounts which are known as *quanta*. Once the molecule has a given number of kinetic energy quanta, these can be apportioned amongst the three directions of motion in many different ways, each resulting in a distinct total *velocity state* for the molecule. The greater the number of quanta, (that is, the greater the total kinetic energy of the molecule) the greater the number of possible velocity states. If we assume that all velocity states are equally probable, then simple statistics predicts that higher velocities will be more favored because there are more higher velocity states.

Although higher kinetic energies are more probable statistically, there is only so much kinetic energy available to the gas as a whole; every molecule that acquires kinetic energy in a collision leaves behind another molecule having less. This tends to even out the kinetic energies in a collection of molecules, and ensures that there are always some molecules whose instantaneous velocity is near zero. The net effect of these two opposing tendencies, one favoring high kinetic energies and the other favoring low ones, is the peaked curve of Fig. 5. At higher temperatures (or with lighter molecules) the latter constraint becomes less important, and the mean velocity increases, but with a wider velocity distribution, the number of molecules having any one velocity diminishes, so the curve tends to flatten out.

Derivation of the Ideal Gas Equation

The ideal gas equation of state came about by combining the empirically determined laws of Boyle, Charles, and Avogadro, but one of the triumphs of the kinetic molecular theory was the derivation of this equation from simple mechanics in the late nineteenth century. This is a beautiful example of how the principles of elementary mechanics can be applied to a simple model to develop a useful description of the behavior of macroscopic matter, and it will be worth your effort to follow and understand the derivation.

⁶This relation was first worked out around 1850 by the great Scottish physicist, James Clerk Maxwell, who is better known for discovering the laws of electromagnetic radiation. Later, Ludwig Boltzmann put the relation on a sounder theoretical basis and simplified the mathematics somewhat.

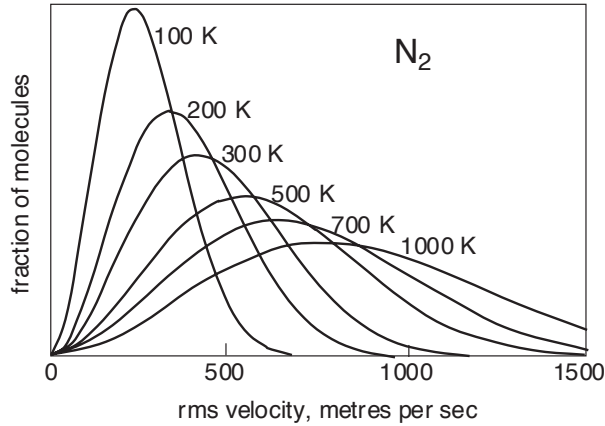


Figure 5: Maxwell-Boltzmann distribution curves

Notice that because of the asymmetry of this curve, the *mean* (rms average) velocity is not the same as the *most probable* velocity, which is defined by the peak of the curve.

We begin by recalling that the pressure of a gas arises from the force exerted when molecules collide with the walls of the container. This force can be found from Newton's law

$$f = ma = m \frac{dv}{dt} \quad (9)$$

in which v is the velocity component of the molecule in the direction perpendicular to the wall.

To evaluate the derivative, which is the velocity change per unit time, consider a single molecule of a gas contained in a cubic box of length l . For simplicity assume that the molecule is moving along the x -axis which is perpendicular to a pair of walls, so that it is continually bouncing back and forth between the same pair of walls. When the molecule of mass m strikes the wall at velocity v_x (and thus with a momentum mv_x) it will rebound elastically and end up moving in the opposite direction with momentum $-mv_x$. The total change in momentum per collision is thus $2mv_x$. After the collision the molecule must travel a distance l to the opposite wall, and then back across this same distance before colliding again with the wall in question. This determines the time between successive collisions with a given wall; the number of collisions per second will be $v_x/2l$. The *force* exerted on the wall is the rate of change of the momentum, given by the product of the momentum change per collision and the collision frequency:

$$\text{force per molecule} = f \equiv \frac{d(mv_x)}{dt} = (2mv_x) \left(\frac{v_x}{2l} \right) = \frac{mv_x^2}{l} \quad (10)$$

Pressure is force per unit area, so the pressure exerted by the molecule on the

wall of cross-section l^2 becomes

$$\text{pressure per molecule} = \frac{mv_x^2}{l^3} = \frac{mv_x^2}{V} \quad (11)$$

in which V is the volume of the box.

We have calculated the pressure due to a single molecule moving at a constant velocity in a direction perpendicular to a wall. If we now introduce more molecules, we must interpret v^2 as the rms-average $\overline{v^2}$. Also, since the molecules are moving randomly in all directions, only one-third of their total velocity will be directed along any one cartesian axis, so the total pressure exerted by N molecules becomes

$$P = \frac{N}{3} \frac{\overline{mv^2}}{V} \quad (12)$$

in which V is the volume of the container.

Recalling that $\frac{mv^2}{2}$ is the average translational kinetic energy ϵ , we can rewrite the above as

$$PV = \frac{1}{3} N m \overline{v^2} = \frac{2}{3} N \epsilon \quad (13)$$

We know that the average kinetic energy is directly proportional to the temperature, so that for a single molecule,

$$\bar{\epsilon} = \frac{\overline{mv^2}}{2} = \frac{3}{2} kT \quad (14)$$

in which the proportionality constant k is known as the *Boltzmann constant*. For one mole of molecules we express this proportionality constant as $N_A k \equiv R$, in which R is the familiar *gas constant*. Substituting into Eq 13 yields the ideal gas equation

$$PV = RT \quad (15)$$

From Eq 13 it is apparent that the product RT has the dimensions of energy, and it in fact represents the average translational kinetic energy per mole. This means that the PV term, and thus its unit, the litre-atmosphere, is also an energy unit. The relationship between the two kinds of units can be obtained by recalling that 1 atm is $1.01325 \times 10^5 \text{ N m}^{-2}$, so that

$$1 \text{ litre atm} = 1000 \text{ cm}^3 \left(\frac{1 \text{ m}^3}{10^6 \text{ cm}^3} \right) \times 1.01325 \times 10^5 \text{ N m}^2 = 101.325 \text{ J} \quad (16)$$

The gas constant R is one of the most important fundamental constants relating to the macroscopic behavior of matter. It is commonly expressed in both pressure-volume and in energy units:

$$R = 0.082057 \text{ litre atm mol}^{-1} \text{ K}^{-1} = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

Notice that the Boltzmann constant k , which appears in many expressions relating to the statistical treatment of molecules, is just $R \div 6.02 \times 10^{23}$, the gas constant per molecule.

How far does a molecule travel between collisions?

Molecular velocities in gases tend to be very high by our everyday standards. This rapid, random motion inevitably results in frequent collisions between molecules. The average distance a molecule moves between such collisions is called the *mean free path*. This distance, denoted by λ , depends on the number of molecules per unit volume and on their size. To avoid collision, a molecule of diameter σ must trace out a path corresponding to the axis of an imaginary cylinder whose cross-section is $\pi\sigma^2$. The volume of the cylinder is $\pi\sigma^2\lambda$. At each collision the molecule is diverted to a new path and traces out a new exclusion cylinder. After colliding with all n molecules in one cubic centimetre of the gas it will have traced out a total exclusion volume of $\pi n\sigma^2\lambda = 1 \text{ cm}^3$. Solving for λ and applying a correction factor $\sqrt{2}$ to take into account exchange of momentum between the colliding molecules (the detailed argument for this is too complicated to go into here), we obtain

$$\lambda = \frac{1}{\sqrt{2}\pi n\sigma^2} \quad (17)$$

Small molecules such as He, H₂, N₂ and CH₄ typically have diameters of around 30-50 nm. At STP the value of n , the number of molecules per cubic metre, is

$$\frac{6.02 \times 10^{23} \text{ mol}^{-1}}{22.4 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}} = 2.69 \times 10^{25}$$

Substitution into Eq 17 yields a value of around 10^{-7} m (100 nm) for most molecules under these conditions. Although this may seem like a very small distance, it typically amounts to 100 molecular diameters, and more importantly, about 30 times the average distance between molecules. This explains why such gases conform very closely to the ideal gas law at ordinary temperatures and pressures.

On the other hand, at each collision the molecule can be expected to change direction. Because these changes are random, the net change in location a molecule experiences during a period of one second is typically rather small. Thus in spite of the high molecular velocities, the speed of molecular *diffusion* in a gas is usually quite small.

The ionosphere and radio communication

At very low pressures, mean free paths are sufficiently great that collisions between molecules become rather infrequent. Under these conditions, highly reactive species such as ions, atoms, and molecular fragments that would ordinarily be destroyed on every collision can persist for appreciable periods of time. The most important example of this occurs at the top of the Earth's atmosphere, at an altitude of 200 km, where the pressure is about 10^{-7} atm .

Here the mean free path will be 10^7 times its value at 1 atm, or about 1 m. In this part of the atmosphere, known as the *thermosphere*, the chemistry is dominated by species such as O, O_2^+ and HO which are formed by the action of intense solar ultraviolet light on the normal atmospheric gases near the top of the stratosphere. The high concentrations of electrically charged species in these regions (sometimes also called the *ionosphere*) reflect radio waves and are responsible for around-the-world transmission of mid-frequency radio signals.

The ion density in the lower part of the ionosphere (about 80 km altitude) is so high that the radiation from broadcast-band radio stations is absorbed in this region before these waves can reach the reflective high-altitude layers. However, the pressure in this region (known as the D-layer) is great enough that the ions recombine soon after local sunset, causing the D-layer to disappear and allowing the waves to reflect off of the upper (F-layer) part of the ionosphere. This is the reason that distant broadcast stations can only be heard at night.

Light bulbs An interesting application involving several aspects of the kinetic molecular behavior of gases is the use of a gas, usually argon, to extend the lifetime of incandescent lamp bulbs. As a light bulb is used, tungsten atoms evaporate from the filament and condense on the cooler inner wall of the bulb, blackening it and reducing light output. As the filament gets thinner in certain spots, the increased electrical resistance results in a higher local power dissipation, more rapid evaporation, and eventually the filament breaks.

The pressure inside a lamp bulb must be sufficiently low for the mean free path of the gas molecules to be fairly long; otherwise heat would be conducted from the filament too rapidly, and the bulb would melt. (Thermal conduction depends on intermolecular collisions, and a longer mean free path means a lower collision frequency). A complete vacuum would minimize heat conduction, but this would result in such a long mean free path that the tungsten atoms would rapidly migrate to the walls, resulting in a very short filament life and extensive bulb blackening.

Around 1910, the General Electric Company hired Irving Langmuir as one of the first chemists to be employed as an industrial scientist in North America. Langmuir quickly saw that bulb blackening was a consequence of the long mean free path of vaporized tungsten molecules, and showed that the addition of a small amount of argon will reduce the mean free path, increasing the probability that an outward-moving tungsten atom will collide with an argon atom. A certain proportion of these will eventually find their way back to the filament, partially reconstituting it. Krypton would be a better choice of gas than argon, since its greater mass would be more effective in changing the direction of the rather heavy tungsten atom. Unfortunately, krypton, being a rarer gas, is around 50 times as expensive as argon, so it is used only in “premium” light bulbs.

Density fluctuations: Why is the sky blue?

Although each molecule in a gas moves randomly, this very randomness ensures that the molecules will quickly distribute themselves throughout the volume occupied by the gas in a thoroughly uniform manner. The chances are virtually zero that sufficiently more molecules might momentarily find themselves near one side of a container than the other to result in an observable temporary density or pressure difference.

This is a result of simple statistics. But statistical predictions are only valid when the sample population is large. Consider what would happen if we consider extremely small volumes of space: cubes that are about 10^{-7} cm on each side, for example? Such a cell would contain only a few molecules, and at any one instant we would expect to find some containing more or less than others, although in time they would average out to the same value. The effect of this statistical behavior is to give rise to random fluctuations in the density of a gas over distances comparable to the dimensions of visible light waves. When light passes through a medium whose density is non-uniform, some of the light is *scattered*. The kind of scattering due to random density fluctuations is called *Rayleigh scattering*, and it has the property of affecting (scattering) shorter wavelengths more effectively than longer wavelengths.

The clear sky appears blue in color because the blue (shorter wavelength) component of sunlight is scattered more. The longer wavelengths remain in the path of the sunlight, available to delight us at sunrise or sunset.

Tyndall scattering If the air contains larger particles such as water droplets, ice crystals, dust, or other particulate matter whose dimensions are greater than those of visible light, another form of scattering occurs. In Tyndall scattering, all colors are scattered equally, and light rays spread out, so the result is a whitish haze and reduced visibility of distant objects.

Distribution of gas molecules in a gravitational field

Everyone knows that the air pressure decreases with altitude. This effect is easily understood qualitatively through the kinetic molecular theory. Random thermal motion tends to move gas molecules in all directions equally. In the presence of a gravitational field, however, motions in a downward direction are slightly favored. This causes the concentration, and thus the pressure of a gas to be greater at lower elevations and to decrease without limit at higher elevations.

Since heavier molecules will be more strongly affected by gravity, their concentrations will fall off more rapidly with elevation. For this reason the partial pressures of the various components of the atmosphere will tend to vary with altitude. The difference in pressure is also affected by the temperature; at higher temperatures there is more thermal motion, and hence a less rapid fall-off of

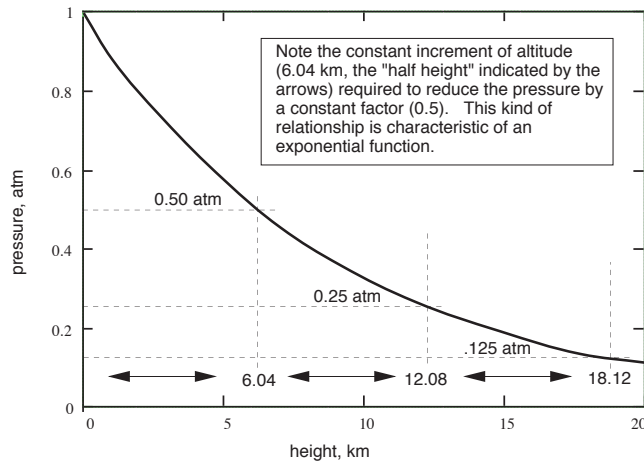


Figure 6: Decrease of pressure with altitude for air at 25 °C

pressure with altitude. Because of atmospheric convection and turbulence, these effects are not observed in the lower part of the atmosphere, but in the uppermost parts of the atmosphere the heavier molecules do tend to drift downward.

The exact functional relationship between pressure and altitude is known as the *barometric distribution law*. It is easily derived using first-year calculus. For air at 25 °C the pressure P_h at any altitude h is given by

$$P_h = P_o e^{-.11h}$$

in which P_o is the pressure at altitude zero. This is a form of the very common *exponential decay law* which we will encounter in several different contexts in this course. An exponential decay (or growth) law describes any quantity whose rate of change is directly proportional to its current value, such as the amount of money in a compound-interest savings account or the density of a column of gas at any altitude. The most important feature of any quantity described by this law is that the fractional rate of change of the quantity in question (in this case, $\Delta P/P$ or in calculus, dP/P) is a constant. This means that the increase in altitude required to reduce the pressure by half is also a constant, about 6 km in the present case.

6 Real gases: deviations from ideal behavior

A plot of PV as a function of the pressure of an ideal gas yields a horizontal straight line. This implies that any increase in the pressure of the gas is exactly counteracted by a decrease in the volume.

Effects of intermolecular repulsions We know, however, that this relation cannot always be valid; a gas cannot be squeezed out of existence. As a gas is compressed, the individual molecules begin to get in each other's way, giving rise to a very strong *repulsive force* acts to oppose any further volume decrease. We would therefore expect the PV -vs.- P line to curve upward at high pressures, and this is in fact what is observed for all gases.

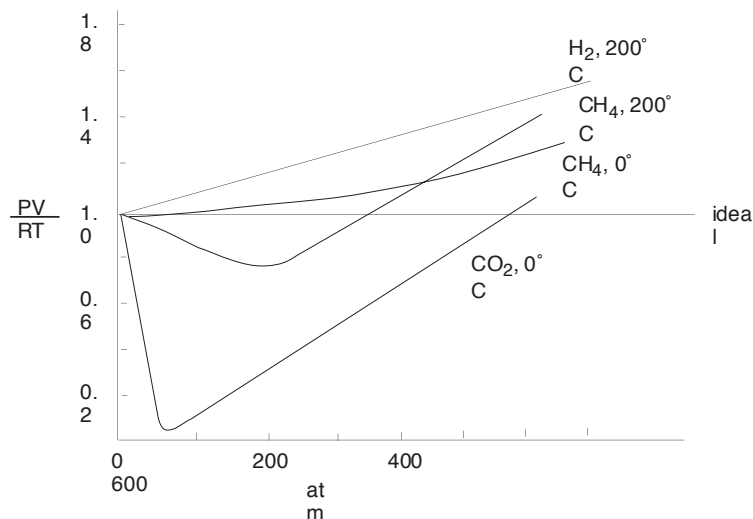
Effects of intermolecular attractions At very close distances, all molecules repel each other as their electron clouds come into contact. At greater distances, however, brief statistical fluctuations in the distribution these electron clouds give rise to a universal attractive force between all molecules. The more electrons in the molecule (and thus the greater the molecular weight), the greater is this attractive force. As long as the energy of thermal motion dominates this attractive force, the substance remains in the gaseous state, but at sufficiently low temperatures the attractions dominate and the substance condenses to a liquid or solid.

The universal attractive force described above is known as the *dispersion*, or *London* force. There may also be additional (and usually stronger) attractive forces related to charge imbalance in the molecule or to hydrogen bonding. These various attractive forces are often referred to collectively as *van der Waals forces*.

The effect of intermolecular attractions on the PV -vs.- P plot would be to hold the molecules slightly closer together, so that the volume would decrease more rapidly than the pressure increases. The resulting curve would dip downward as the pressure increases, and this dip would be greater at lower temperatures and for heavier molecules. At higher pressures, however, the stronger repulsive forces would begin to dominate, and the curve will eventually bend upward as before.

The effects of intermolecular interactions are most evident at low temperatures and high pressures; that is, at high *densities*. As the pressure approaches zero, the behavior of any gas will conform more and more closely to the ideal gas equation of state, which should really be depicted as a *limiting* relation

$$\lim_{P \rightarrow 0} PV = nRT \quad (18)$$

Figure 7: PV -vs- P plots for real gases

Equations of state for real gases

How might we modify the ideal gas equation of state to take into account the effects of intermolecular interactions? The first and most well known answer to this question was offered by the Dutch scientist J.D. van der Waals in 1873.

van der Waals recognized that the molecules themselves take up space that subtracts from the volume of the container, so that the “volume of the gas” V in the ideal gas equation should be replaced by the term $(V - b)$ where b is the *excluded volume*, typically of the order of $20\text{-}100\text{ cm}^3\text{ mol}^{-1}$.

The intermolecular attractive forces act to slightly diminish the frequency and intensity of encounters between the molecules and the walls of the container; the effect is the same as if the pressure of the gas were slightly higher than it actually is. This imaginary increase is called the *internal pressure*, and we can write

$$P_{\text{effective}} = P_{\text{ideal}} - P_{\text{internal}}$$

Thus we should replace the P in the ideal gas equation by

$$P_{\text{ideal}} = P_{\text{effective}} + P_{\text{internal}}$$

Since the attractions are between pairs of molecules, the total attractive force is proportional to the square of the number of molecules per volume of space, and thus for a fixed number of molecules such as one mole, the force is *inversely* proportional to the square of the volume of the gas; the smaller the volume, the closer are the molecules and the greater the attractions between

pairs (hence the square term) of molecules. The pressure that goes into the corrected ideal gas equation is

$$P_{\text{ideal}} = P + \frac{a}{V^2}$$

in which the constant a expresses the magnitude of the attractive forces in a particular gas and has a value of 10^6 - 10^7 atm cm⁶ mol⁻².

The complete van der Waals equation of state thus becomes

$$\left(P + \frac{a}{V^2}\right)(V - b) = nRT \quad (19)$$

Although you do not have to memorize this equation, you are expected to understand it and to explain the significance of the terms it contains. You should also understand that the van der Waals constants a and b must be determined empirically for every gas. This can be done by plotting the P - V behavior of the gas and adjusting the values of a and b until the van der Waals equation results in an identical plot. The constant a is related in a simple way to the molecular radius; thus the determination of a constitutes an indirect measurement of an important microscopic quantity.

The van der Waals equation is only one of many equations of state for real gases. More elaborate equations are required to describe the behavior of gases over wider pressure ranges. These generally take account of higher-order nonlinear attractive forces, and require the use of more empirical constants. Although we will make no use of them in this course, they are widely employed in engineering work in which the behavior of gases at high pressures must be accurately predicted.

The most striking feature of real gases is that they cease to remain gases as the temperature is lowered and the pressure is increased. The graphs in Fig. 8 illustrate this behavior; as the volume is decreased, the lower-temperature isotherms suddenly change into straight lines. Under these conditions, the pressure remains constant as the volume is reduced. This can only mean that the gas is “disappearing” as we squeeze the system down to a smaller volume. In its place, we obtain a new state of matter, the liquid. In the shaded region of Fig. 8 on the right, *two* phases, liquid, and gas, are simultaneously present. Finally, at very small volume all the gas has disappeared and only the liquid phase remains. At this point the isotherms bend strongly upward, reflecting our common experience that a liquid is practically incompressible.

The maximum temperature at which the two phases can coexist is called the *critical temperature*. The set of (P, V, T) corresponding to this condition is known as the *critical point*. Liquid and gas can coexist only within the regions indicated in Fig. 8 by the wedge-shaped cross section on the left and the shaded area on the right. An important consequence of this is that *a liquid phase cannot exist at temperatures above the critical point*.

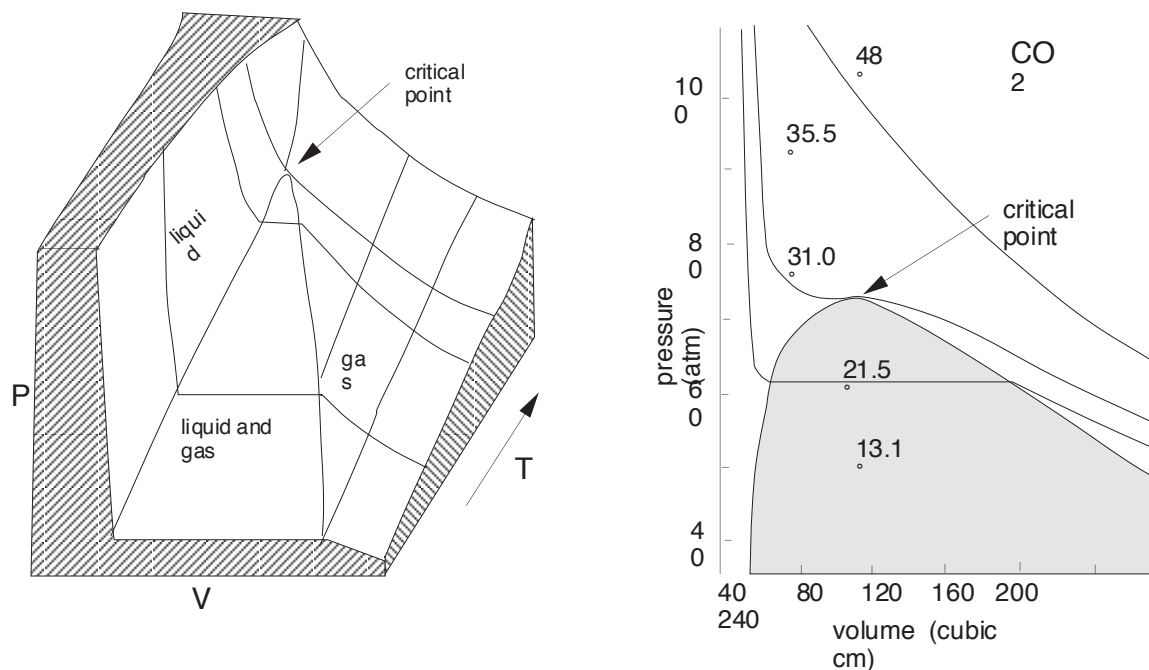


Figure 8: Critical behavior of a real gas

The critical temperature of carbon dioxide is $31\text{ }^{\circ}\text{C}$, so you can tell whether the temperature is higher or lower than this by shaking a CO_2 fire extinguisher; on a warm day, you will not hear any liquid sloshing around inside. The critical temperature of water is $374\text{ }^{\circ}\text{C}$, and that of hydrogen is only $33\text{ }^{\circ}\text{K}$.

If the region of the almost-vertical isotherms represents the liquid, what is the state of the substance near the left side of either plot, but above the critical point? The answer is that it is a highly-nonideal gas, perhaps best described just as a “fluid”—but certainly not a liquid. One intriguing consequence of the very limited bounds of the liquid state is that you could start with a gas at large volume and low temperature, raise the temperature, reduce the volume, and then reduce the temperature so as to arrive at the liquid region at the lower left, without ever passing through the two-phase region, and thus *without undergoing condensation!*

The *supercritical* state of matter, as the fluid above the critical point is often called, possesses the flow properties of a gas and the solvent properties of a liquid. Supercritical carbon dioxide is now used to dissolve the caffeine out of coffee beans, and supercritical water has recently attracted interest as a medium for chemically decomposing dangerous environmental pollutants such as PCBs.

substance	T_b ($^{\circ}\text{K}$)	T_c ($^{\circ}\text{K}$)	P_c (atm)	V_c (ml mol^{-1})
Helium	4.2	5.3	2.3	57.8
Hydrogen	20.4	33.2	12.8	65.0
Neon	27.1	44.5	26.9	41.7
Nitrogen	77.3	126	34.5	93.1
Carbon monoxide	81.7	133	34.5	93.1
Oxygen	90.2	155	50.1	74.4
Carbon dioxide	-	304	72.9	94.0
Ammonia	240	405	111	72.1
Benzene	353	563	48.6	260
Water	373	647	218	55.3

Table 1: Critical constants of some common substances