

# Properties of Gases

*Introduction to the ideal gas laws, kinetic-molecular theory and real gases*

A Chem1 Virtual Textbook *chapter*

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**About this document:**

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# 1 • Introduction: observable properties of gases

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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 Effluvi-ums*”.

It's interesting, however, that around 550 BCE the Greek philosopher Anaximenes maintained that all matter consists of air: “*It is from air that all the things that exist, have existed, or will exist come into being.*”

The invention of the sensitive *balance* in the early seventeenth century showed once and for all that gases have weight and are therefore matter. Guericke's invention of the air pump (which led directly to his discovery of the vacuum) launched the “pneumatic era” of chemistry long before the existence of atoms and molecules had been accepted. Indeed, the behavior of gases was soon to prove an invaluable tool in the development of the atomic theory of matter.

The study of gases allows us to understand the behavior of matter at its simplest: individual particles, 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) in which the theory of gases will no longer give us correct answers, but it will still provide us with a useful model that will at least help us to rationalize the behavior of these more complicated states of matter.

## 1.1 What's special about gases?

Let us start with what we can observe experimentally about gases.

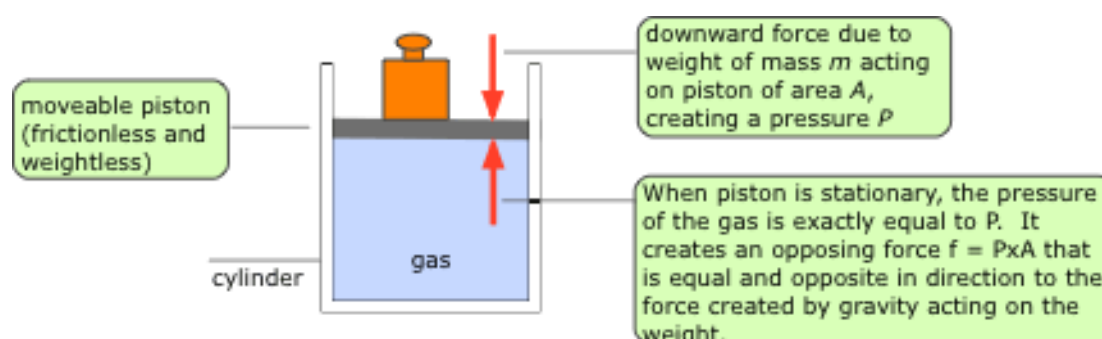
- First, we know that a gas has **no definite volume or shape**; a gas will fill whatever volume is available to it. Contrast this to the behavior of a liquid, which always has a distinct upper surface when its volume is less than that of the space it occupies.
- The other outstanding characteristic of gases is their **low densities**, compared with those of liquids and solids. One mole of liquid water at 298 K and 1 atm pressure occupies a volume of 18.8 cm<sup>3</sup>, whereas the same quantity of water vapor at the same temperature and pressure has a volume of 30200 cm<sup>3</sup>, 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.

We will see later that each of these three macroscopic characteristics of gases follows directly from the microscopic view— that is, from the *atomic* nature of matter.

## 1.2 The pressure of a gas

The molecules of a gas, being in continuous motion, frequently strike the inner walls of their container. As they do so, they immediately bounce off without loss of kinetic energy, but the reversal of direction (*acceleration*) imparts a *force* to the container walls. This force, divided by the total surface area on which it acts, is the *pressure* of the gas.

The pressure of a gas is observed by measuring the pressure that must be applied externally in order to keep the gas from expanding or contracting. 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 (more precisely, a *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.



### Pressure units

The unit of pressure in the SI system is the pascal (Pa), defined as a force of one newton per square metre ( $1 \text{ Nm}^{-2} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$ .)

At the Earth's surface, the force of gravity acting on a 1 kg mass is 9.81 N. Thus if, in the above Figure, the weight is 1 kg and the surface area of the piston is 1 M, the pressure of the gas would be 9.81 Pa. A 1-gram weight acting on a piston of 1 cm<sup>2</sup> cross-section would exert a pressure of 98.1 pA. (If you wonder why the pressure is higher in the second example, consider the number of cm<sup>2</sup> contained in 1 m<sup>2</sup>.)

In chemistry, it is more common to express pressures in units of atmospheres or torr:  
 $1 \text{ atm} = 101325 \text{ Pa} = 760 \text{ torr}$ .

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 still widely used; standard atmospheric pressure is 14.7 psi.

## How is pressure measured?

**Atmospheric pressure and the barometer** The column of air above us exerts a force on each  $1\text{-cm}^2$  of surface equivalent to a weight of about 1034 g.

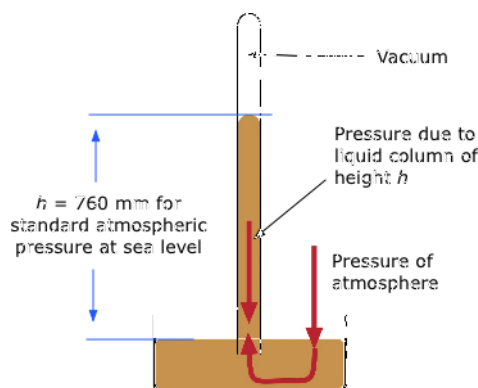
This figure is obtained by solving Newton's law  $f = ma$  for  $m$ , using the acceleration of gravity for  $a$ :

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

So, if several kilos of air are constantly pressing down on your body, why do you not feel it?

*Answer:* because every other part of your body (including within your lungs and insides) also experiences the same pressure, so there is no net force (other than gravity) acting on you.

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.



How is the air pressure of  $1034 \text{ g cm}^{-3}$  related to the 760-mm height of the mercury column in the barometer? What if water were used in place of mercury?

*Answer:* The density of Hg is  $13.6 \text{ g cm}^{-3}$ , so in a column of  $1\text{-cm}^2$  cross-section, the height needed to counter the atmospheric pressure would be  $(1034 \text{ g} / 1 \text{ cm}^2) / (13.6 \text{ g cm}^{-3}) = 76 \text{ cm}$ .

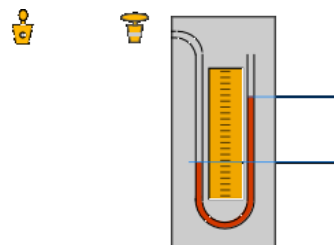
The density of water is only  $1/13.6$  that of mercury, so standard atmospheric pressure would support a water column whose height is  $13.6 \times 76 \text{ cm} = 1034 \text{ cm}$ , or 10.3 m. You would have to read a water barometer from a fourth-story window!

Torricelli's invention overturned the then-common belief that air (and by extension, all gases) are weightless.

The fact that we live at the bottom of a sea of air was most spectacularly demonstrated in 1654, when two teams of eight horses were unable to pull apart two 14-inch copper hemispheres (the "Magdeburg hemispheres") which had been joined together and then evacuated with Guericke's newly-invented vacuum pump.

## The 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.



### 1.3 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.

At one point in the 18th century, 35 different temperature scales were in use!

The *Celsius* temperature scale locates the zero point at the freezing temperature of water; the Celsius degree ( $^{\circ}\text{C}$ )<sup>1</sup> 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 the coldest temperature it was possible to obtain at the time (by mixing salt and ice.) The 100° point was set with body temperature (later found to be 98.6°F.) 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  $1^{\circ}\text{F} = 9/5^{\circ}\text{C}$ . 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 size.

You should be able to derive the formula for this conversion.

#### 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 the gas will diminish by 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°C. 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 sizes 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°, is about 293 K.

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1. Notice that temperature is expressed by placing the degree symbol in front of the scale abbreviation ( $37^{\circ}\text{C}$ ), whereas a temperature *interval* is written with the degree sign following the symbol ( $2^{\circ}\text{C}$ ).

A rather fine point to note: the degree symbol is not used with the "K", which should always be separated from the preceding number by a space. See here for an explanation.

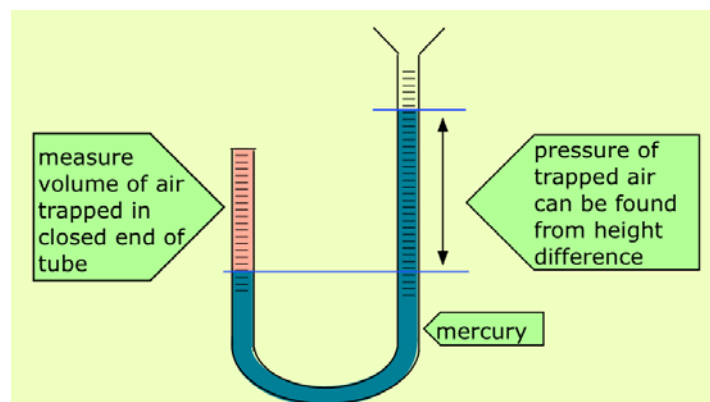
Because the Kelvin scale is based on an absolute, rather than on an arbitrary zero of temperature, it plays a special significance in scientific calculations; most fundamental physical relations involving temperature are expressed mathematically in terms of absolute temperature. In engineering work, an absolute scale based on the Fahrenheit degree is sometimes used; this is known as the *Rankine* scale.

## 2 • The basic gas laws

The "pneumatic" era of chemistry began with the discovery of the vacuum around 1650 which clearly established that gases are a form of matter. The ease with which gases could be studied soon led to the discovery of numerous empirical (experimental) laws that proved fundamental to the later development of chemistry and led indirectly to the atomic view of matter.

### 2.1 Pressure-volume relations: Boyle's law

ROBERT BOYLE (1627-91) 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.



volume	pressure	P×V
96.0	2.00	192
76.0	2.54	193
46.0	4.20	193
26.0	7.40	193

Some of Boyle's actual data showing the constancy of the *PV* product

The effect can be seen in a simple J-shaped tube in which air is trapped in the short limb as mercury is poured into the right side. The difference between the heights of the two mercury columns gives the pressure (76 cm = 1 atm), and the volume of the air is calculated from the length of the air column and the tubing diameter. In Boyle's experiment he used a simple air pump invented by his friend Robert Hooke.

*Boyle's law* can be expressed as

$$PV = \text{constant} \quad (1)$$

or, equivalently,

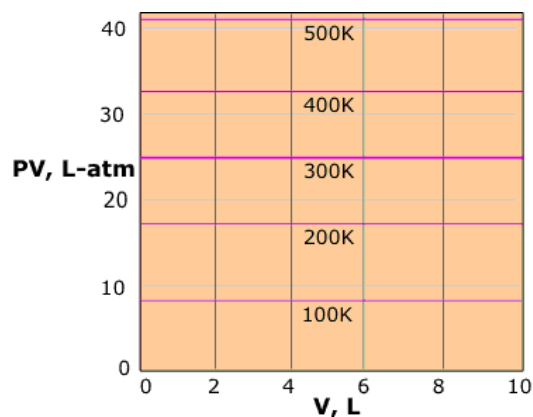
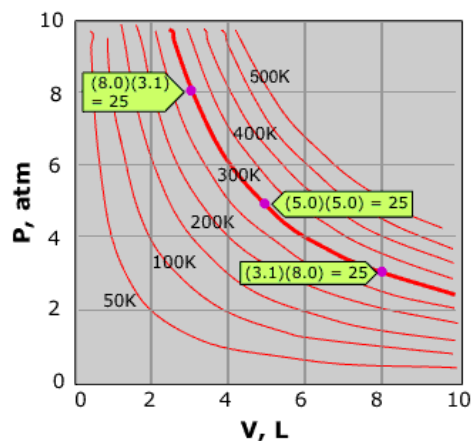


$$P_1V_1 = P_2V_2 \quad (2)$$

These relations hold true only if the number of molecules  $n$  and the temperature are constant. This is a relation 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. There will be a separate  $P$ - $V$  plot for each temperature; a single  $P$ - $V$  plot is therefore called an *isotherm*.

Shown here are some isotherms for one mole of an ideal gas at several different temperatures. Each plot has the shape of a *hyperbola*—the locus of all points having the property  $xy = a$ , where  $a$  is a constant. You will see later how the value of this constant ( $PV=25$  for the 300K isotherm shown here) is determined.

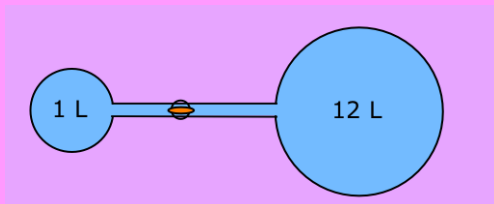
It is very important that you understand this kind of plot which governs any relationship of inverse proportionality. You should be able to sketch out such a plot when given the value of any one  $(x,y)$  pair.



A related type of plot with which you should be familiar shows the product  $PV$  as a function of the pressure. You should understand why this yields a straight line, and how this set of plots relates to the one immediately above.

**Problem Example 1**

In an industrial process, a gas confined to a volume of 1 L at a pressure of 20 atm is allowed to flow into a 12-L container by opening the valve that connects the two containers. What will be the final pressure of the gas?



Solution: The final volume of the gas is  $(1 + 12)\text{L} = 13\text{ L}$ . The gas expands in inverse proportion to the two volumes:

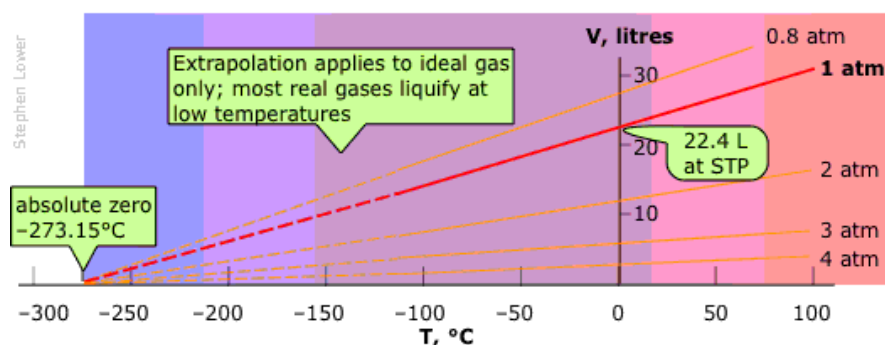
$$P_2 = (20\text{ atm}) \times (1\text{ L} / 13\text{ L}) = 1.5\text{ atm}$$

Note that there is no need to make explicit use of any “formula” in problems of this kind!

## 2.2 How the temperature affects the volume: Charles' law

All matter expands when heated, but gases are special in that their degree of expansion is independent of their composition. The French scientists JACQUES CHARLES (1746-1823) and JOSEPH GAY-LUSSAC (1778-1850) independently found that if the pressure is held constant, the volume of any gas changes by the same fractional amount ( $1/273$  of its value) for each  $^{\circ}\text{C}$  change in temperature.

The volume of a gas confined against a constant pressure is directly proportional to the absolute temperature.



A graphical expression of the law of Charles and Gay-Lussac can be seen in these plots of the volume of one mole of an ideal gas as a function of its temperature at various constant pressures.

- *What do these plots show?* The straight-line plots show that the ratio  $V/T$  (and thus  $dV/dT$ ) is a constant at any given pressure. Thus we can express the law algebraically as  $V/T = \text{constant}$  or  $V_1/T_1 = V_2/T_2$ . (Don't memorize this formula!)
- *What is the significance of the extrapolation to zero volume?* If a gas contracts by  $1/273$  of its volume for each degree of cooling, it should contract to zero volume at a temperature of  $-273^{\circ}\text{C}$ . This, of course, is the absolute zero of temperature, and this extrapolation of Charles' law is the first evidence of the special significance of this temperature.
- *Why do the plots for different pressures have different slopes?* The lower the pressure, the greater the volume (Boyle's law), so at low pressures the fraction  $(V/273)$  will have a larger value. You might say that the gas must "contract faster" to reach zero volume when its starting volume is larger.

### Problem Example 2

The air pressure in a car tire is 30 psi (pounds per square inch) at  $10^{\circ}\text{C}$ . What will the pressure be after driving has raised its temperature to  $45^{\circ}\text{C}$ ? (Assume that the volume remains unchanged.)

*Solution:* The gas expands in direct proportion to the ratio of the absolute temperatures:

$$P_2 = (30 \text{ psi}) \times (318\text{K} / 283\text{K}) = 33.7 \text{ psi}$$

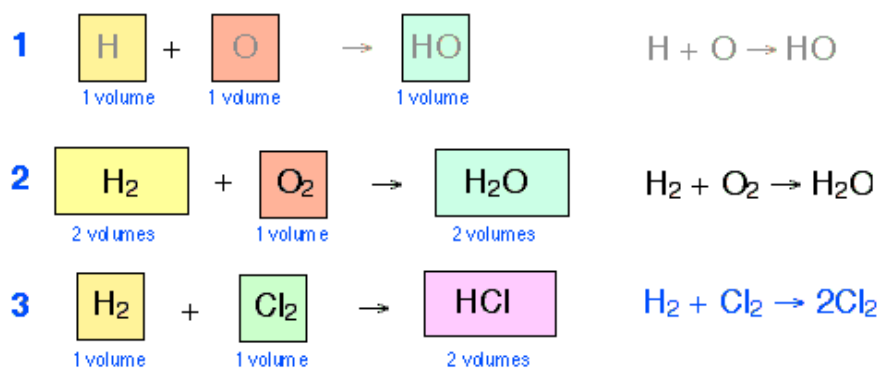
## 2.3 Volume and the number of molecules: Avogadro's law

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 (1776-1856) drew the crucial conclusion: these volume ratios must be related to the relative numbers of molecules that react, and thus the famous "*E. V. E. N principle*":

Equal volumes of gases measured at the same temperature and pressure contain equal numbers of molecules

Avogadro's law thus predicts a *directly proportional* relation between the number of moles of a gas and its volume.

This relationship, originally known as *Avogadro's Hypothesis*, was crucial in establishing the formulas of simple molecules at a time (around 1811) when the distinction between atoms and molecules was not clearly understood. In particular, the existence of diatomic molecules of elements such as  $H_2$ ,  $O_2$ , and  $Cl_2$  was not recognized until the results of combining-volume experiments such as those depicted below could be interpreted in terms of the E.V.E.N. principle.



Once it was shown that equal volumes of hydrogen and oxygen do not combine in the manner depicted in **(1)**, it became clear that these elements exist as diatomic molecules and that the formula of water must be  $H_2O$  rather than  $HO$  as previously thought.

## 2.4 The ideal gas equation of state

If the variables  $P$ ,  $V$ ,  $T$  and  $n$  (the number of moles) 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*. By combining the expressions of Boyle's, Charles', and Avogadro's laws (you should be able to do this!) we can write the very important *ideal gas equation of state*

$$PV = nRT$$

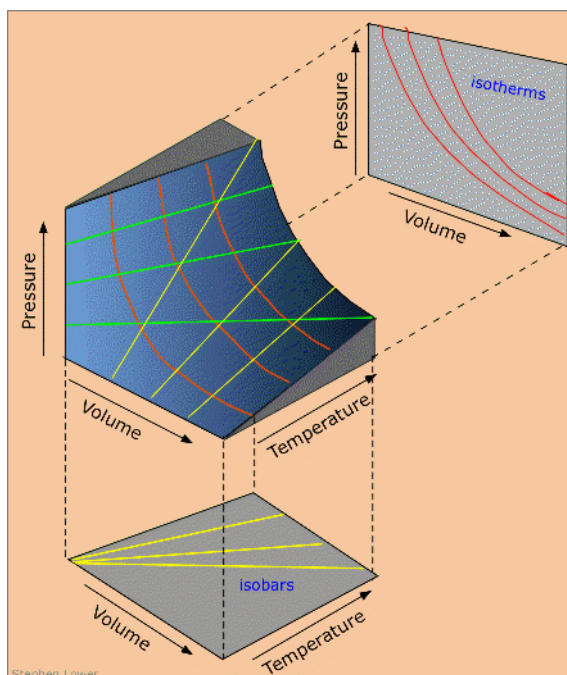
**Must know this!**

in which 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.

In order to depict the relations between the three variables  $P$ ,  $V$  and  $T$  we need a three-dimensional graph.



**Fig. 1: PVT surface for an ideal gas**

Each point on the curved surface represents a possible combination of  $(P, V, T)$  for an arbitrary quantity of 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 red curved lines, being lines of constant temperature, are *isotherms*, and are plots of Boyle's law. These isotherms are also seen projected onto the  $x$ - $y$  plane at the top right. The yellow lines are *isobars* and represent Charles' law plots; they are projected onto the  $x$ - $z$  plane at the bottom.

The green lines, known as *isochors*, show all values of  $(P, V, T)$  with various fixed volumes.

**Problem Example 3**

A biscuit made with baking powder has a volume of 20 mL, of which one-fourth consists of empty space created by gas bubbles produced when the baking powder decomposed to CO<sub>2</sub>. What weight of NaHCO<sub>3</sub> was present in the baking powder in the biscuit? Assume that the gas reached its final volume during the baking process when the temperature was 400°C.

(Baking powder consists of sodium bicarbonate mixed with some other solid that produces an acidic solution on addition of water, initiating the reaction  $\text{NaHCO}_3(\text{s}) + \text{H}^+ \rightarrow \text{Na}^+ + \text{H}_2\text{O} + \text{CO}_2$ )

*Solution:* Use the ideal gas equation to find the number of moles of CO<sub>2</sub> gas; this will be the same as the number of moles of NaHCO<sub>3</sub> (84 g mol<sup>-1</sup>) consumed :

$$n = \frac{(1 \text{ atm})(0.005 \text{ L})}{(0.082 \text{ L atm}^{-1} \text{ mol}^{-1})(673 \text{ K})} = 9.1\text{E-}6 \text{ mol}$$

$$9.1\text{E-}6 \text{ mol} \times 84 \text{ g mol}^{-1} = 0.0076 \text{ g}$$

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## 3 • Molar volume and density

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Although all gases closely follow the ideal gas law  $PV = nRT$  under appropriate conditions, each gas is also a unique chemical substance consisting of molecular units that have definite masses. In this lesson we will see how these molecular masses affect the properties of gases that conform to the ideal gas law.

Following this, we will look at gases that contain more than one kind of molecule—in other words, *mixtures* of gases.

### 3.1 Molar volume of a gas: standard temperature and pressure

You will recall that the *molar mass* of a pure substance is the mass of  $6.02 \times 10^{23}$  (*Avogadro's number*) of particles or molecular units of that substance. Molar masses are commonly expressed in units of grams per mole (g mol<sup>-1</sup>) and are often referred to as *molecular weights*.

As was explained in the preceding lesson, equal volumes of gases, measured at the same temperature and pressure, contain equal numbers of molecules (this is the "*EVEN*" *principle*, more formally known as *Avogadro's law*.)

This means that one mole of any gas will occupy the same volume as one mole of any other gas at a given temperature and pressure. The magnitude of this volume will of course depend on the temperature and pressure, so as a means of convenient comparison it is customary to define a set of conditions  $T = 273\text{K}$  and  $P = 1\text{atm}$  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*  $22.4\text{L mol}^{-1}$  is a value worth memorizing, but remember that it is valid only at STP. The molar volume at other temperatures and pressures can easily be found by simple proportion.

#### Problem Example 4

What would the volume of one mole of air be at  $20^\circ\text{C}$  on top of Muana Kea, Haw'ail (altitude 4.2 km) where the air pressure is approximately 600 kPa?

*Solution:* Apply Boyle's and Charles' laws as successive correction factors to the standard sea-level pressure of 1013 kPa:

$$V_2 = (22.4\text{ L}) \left( \frac{293\text{K}}{273\text{K}} \right) \left( \frac{1013\text{ kPa}}{620\text{ kPa}} \right) = 36.0\text{ L}$$



The molar volume of a substance can tell us something about how much space each molecule occupies, as the following example shows.

#### Problem Example 5

Estimate the average distance between the molecules in a gas at  $1\text{atm}$  pressure and  $0^\circ\text{C}$ .

*Solution.* Consider a  $1\text{-cm}^3$  volume of the gas, which will contain

$$(6.02\text{E}23\text{ mol}^{-1}) / (22400\text{ cm}^3\text{ mol}^{-1}) = 2.69\text{E}19\text{ cm}^{-3}.$$

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  $3.72\text{E}-20\text{ cm}^3$ . 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:

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

### 3.2 Molecular weight and density of a gas

The molar volumes of all gases are the same when measured at the same temperature and pressure. But the molar masses of different gases will vary. This means that different gases will have different *densities* (different masses per unit volume). If we know the molecular weight of a gas, we can calculate its density.

#### Problem Example 6

Uranium hexafluoride  $\text{UF}_6$  gas is used in the isotopic enrichment of natural uranium. Calculate its density at STP.

*Solution:* The molecular weight of  $\text{UF}_6$  is 352.

$$(352 \text{ g mol}^{-1}) / (22.4 \text{ mol L}^{-1}) = 15.7 \text{ g L}^{-1}$$

*Note:* there is no need to look up a "formula" for this calculation; simply combine the molar mass and molar volume in such a way as to make the units come out correctly.

More importantly, if we can measure the density of an unknown gas, we have a convenient means of estimating its molecular weight. This is one of many important examples of how a *macroscopic* measurement (one made on bulk matter) can yield *microscopic* information (that is, about molecular-scale objects.)

Determination of the molecular weight of a gas from its density 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  $22.4 \text{ mol}^{-1}$  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.

Gas densities are now measured in industry by electro-mechanical devices such as vibrating reeds which can provide continuous, on-line records at specific locations, as within pipelines.

#### Problem Example 7

Calculate the approximate molar mass of a gas whose measured density is 3.33 g/L at  $30^\circ\text{C}$  and 780 torr.

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

$$n = \frac{PV}{RT} = \frac{(780/760) \text{ atm} \times (1.00 \text{ L})}{(0.082 \text{ L atm mol}^{-1}\text{K}^{-1})(393\text{K})} = .0413 \text{ mol}$$

The molecular weight is therefore  $(33 \text{ g L}^{-1}) / (.0413 \text{ mol L}^{-1}) = 80.6 \text{ g mol}^{-1}$

Gas density measurements can be a useful means of estimating the composition of a mixture of two different gases:



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## 4 • Mixtures of gases

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Because most of the volume occupied by a gas consists of empty space, there is nothing to prevent two or more kinds of gases from occupying the same volume. *Homogeneous mixtures* of this kind are generally known as *solutions*, but it is customary to refer to them simply as *gaseous mixtures*.

### 4.1 Mole fractions and volumes

We can specify the composition of gaseous mixtures in many different ways, but the most common ones are by *volumes* and by *mole fractions*. From Avogadro's Law we know that "equal volumes contains equal numbers of molecules", so when we say that air, for example, is 21 percent oxygen and 78 percent nitrogen by volume, this is the same as saying that these same percentages of the molecules in air consist of O<sub>2</sub> and N<sub>2</sub>. Similarly, in 1.0 mole of air, there is 0.21 mol of O<sub>2</sub> and 0.78 mol of N<sub>2</sub> (the other 0.1 mole consists of various of trace gases, but is mostly neon.)

Note that you could never assume a similar equivalence with mixtures of liquids or solids, to which the E.V.E.N. principle does not apply.

These last two numbers (.21 and .78) also express the mole fractions of oxygen and nitrogen in *air*. *Mole fraction* means exactly what it says: the fraction of the molecules that consist of a specific substance. This is expressed algebraically by

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

so in the case of oxygen, its mole fraction is

$$X_{O_2} = \frac{n_{O_2}}{n_{O_2} + n_{N_2} + n_{Ar}} = \frac{.21}{1} = .21$$

Don't let this type of notation put you off! The summation sign  $\sum n_i$  (Greek Sigma) simply means to add up the  $n$ 's (number of moles) of every substance present. Thus if O<sub>2</sub> is the " $i$ -th" substance as in the expression immediately above, the summation runs from  $i=1$  through  $i=3$ .

**Problem Example 8**

A mixture of O<sub>2</sub> and nitrous oxide, N<sub>2</sub>O, is sometimes used as a mild anesthetic in dental surgery. A certain mixture of these gases has a density of 1.482 g L<sup>-1</sup> at 25 and 0.980†atm. What was the mole-percent of N<sub>2</sub>O in this mixture?

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

$$(1.452 \text{ g L}^{-1}) \times \left(\frac{298}{273}\right) \left(\frac{1}{.980}\right) = 1.65 \text{ g L}^{-1}$$

The molar mass of the mixture is (5 g L<sup>-1</sup>)(22.4 L mol<sup>-1</sup>) = 37.0 g mol<sup>-1</sup>. The molecular weights of O<sub>2</sub> and N<sub>2</sub> are 32 and 44, respectively. Thus the fraction of the heavier gas in the mixture is

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

**4.2 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*, a concept invented by the famous English chemist JOHN DALTON (1766-1844). Dalton reasoned that the low density and high compressibility of gases indicates that they consist mostly of empty space; from this it follows that when two or more different gases occupy the same volume, they behave entirely independently.

*"Every gas is a vacuum to every other gas."*

John Dalton

The contribution that each component of a gaseous mixture makes to the total pressure of the gas is known as the partial pressure of that gas. Dalton himself stated this law in the simple and vivid way quoted above. The usual way of stating Dalton's Law of Partial Pressures is

***The total pressure of a gas is the sum of the partial pressures of its components***

This is expressed algebraically as

$$P_{\text{total}} = P_1 + P_2 + \dots = \sum_i P_i$$

or, equivalently,

$$P_{\text{total}} = \frac{RT}{V} \sum_i n_i$$

(If you feel a need to memorize these formulas, you probably don't really understand Dalton's Law!)

### Problem Example 9

What is the mole fraction of carbon dioxide in a mixture consisting of equal masses of CO<sub>2</sub> (MW=44) and neon (MW=20.2)?

*Solution:* Assume any arbitrary mass, such as 100 g, find the equivalent numbers of moles of each gas, and then substitute into the definition of mole fraction:

$$n_{\text{CO}_2} = (100 \text{ g}) / (44 \text{ g mol}^{-1}) = 2.3 \text{ mol}$$

$$n_{\text{Ne}} = (100 \text{ g}) / (20.2 \text{ g mol}^{-1}) = 4.9 \text{ mol}$$

$$X_{\text{Ne}} = (2.3 \text{ mol}) / (2.3 \text{ mol} + 4.9 \text{ mol}) = 0.43$$

### Problem Example 10

Calculate the mass of each component present in a mixture of fluorine (MW 19.0) and xenon (MW†131.3) contained in a 2.0-L flask. The partial pressure of Xe is 350†torr and the total pressure is 724†torr at 25°C.

*Solution:* From Dalton's law, the partial pressure of F<sub>2</sub> is (724 – 350)†=†374 torr:

The mole fractions are  $X_{\text{Xe}} = 350/724 = .48$  and  $X_{\text{F}_2} = 374/724 = .52$ . The total number of moles of gas is

$$n = \frac{PV}{RT} = \frac{(724/760)(2)}{(.082)(298)} = .078 \text{ mol}$$

The mass of Xe is (131.3 g mol<sup>-1</sup>) ∗ (.48 ∗ .078 mol) = 4.9 g

## 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 fractions of each gas, multiplied by the molar mass of that substance.

### Problem Example 11

Find the average molar mass of dry air whose volume-composition is O<sub>2</sub> (21%), N<sub>2</sub> (78%) and Ar (1%).

*Solution:* The average molecular weight is the mole-fraction-weighted sum of the molecular weights of its components. The mole fractions, of course, are the same as the volume-fractions (E.V.E.N. principle.)

$$m_{\text{total}} = \sum_i x_i m_i$$

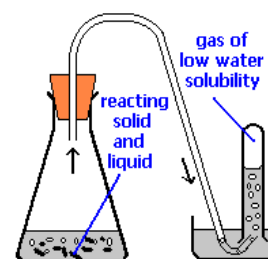
$$m = (.21 \times 32) + (.78 \times 28) + (.01 \times 20) = 28$$

## 4.3 Some applications of Dalton's Law

### Collecting gases over water

A common laboratory method of collecting the gaseous product of a chemical reaction is to conduct it into an inverted tube or bottle filled with water, the opening of which is immersed in a larger container of water. This arrangement is called a pneumatic trough, and was widely used in the early days of chemistry. As the gas enters the bottle it displaces the water and becomes trapped in the upper part.

The volume of the gas can be observed by means of a calibrated scale on the bottle, but what about its pressure? The total pressure confining the gas is just that of the atmosphere transmitting its force through the water. But liquid water itself is always in equilibrium with its vapor, so the space in the top of the tube is a mixture of two gases: the gas being collected, and gaseous H<sub>2</sub>O. The partial pressure of H<sub>2</sub>O is known as the vapor pressure of water and it depends on the temperature. In order to determine the quantity of gas we have collected, we must use Dalton's Law to find the partial pressure of that gas.



**Problem Example 12**

Oxygen gas was collected over water as shown above. The atmospheric pressure was 754 torr, the temperature was 22°C, and the volume of the gas was 155 mL. The vapor pressure of water at 22°C is 19.8 torr. Use this information to estimate the number of moles of O<sub>2</sub> produced.

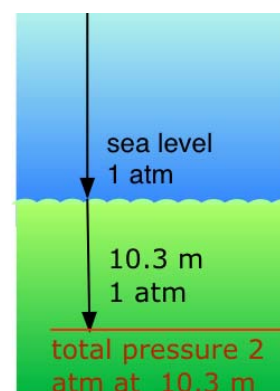
*Solution.* From Dalton's law,  $P_{O_2} = P_{total} - P_{H_2O} = 754 - 19.8 = 734$  torr.

$$n = \frac{PV}{RT} = \frac{(734/760) \text{ atm} \times (0.155 \text{ L})}{.082 \text{ L atm mol}^{-1}\text{K}^{-1}(295\text{K})} = .0413 \text{ mol}$$

**Scuba Diving**

Our respiratory systems are designed to maintain the proper oxygen concentration in the blood when the partial pressure of O<sub>2</sub> is 0.21 atm, its normal sea-level value. Below the water surface, the pressure increases by 1 atm for each 10.3-m increase in depth; thus a scuba diver at 10.3 m experiences a total of 2 atm pressure pressing on the body. In order to prevent the lungs from collapsing, the air the diver breathes should also be at about the same pressure.

But at a total pressure of 2 atm, the partial pressure of O<sub>2</sub> in ordinary air would be 0.42 atm; at a depth of 100 ft (about 30 m), the O<sub>2</sub> pressure of .8 atm would be far too high for health. For this reason, the air mixture in the pressurized tanks that scuba divers wear must contain a smaller fraction of O<sub>2</sub>. This can be achieved most simply by raising the nitrogen content, but high partial pressures of N<sub>2</sub> can also be dangerous owing to its greater tendency to dissolve in the blood, which can create a condition known as *nitrogen narcosis*. The preferred diluting agent for sustained deep diving is helium, which has very little tendency to dissolve in the blood even at high pressures.




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## 5 • Molecules in motion: introduction to kinetic molecular theory

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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 19<sup>th</sup> century the atomic theory of matter was sufficiently well accepted that scientists began to relate these macroscopic properties to the 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 under many conditions it describes the behavior of real gases at ordinary temperatures and pressures quite accurately, and serves as the starting point for dealing with more complicated states of matter.

## 5.1 The kinetic-molecular model

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

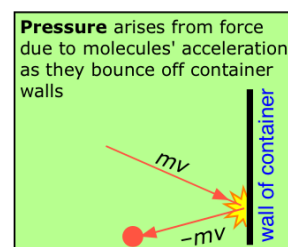
1. A gas is composed of molecules that are separated by average distances that are much greater than the sizes of the molecules themselves. **The volume occupied by the molecules of the gas is negligible compared to the volume of the gas itself.**
2. The molecules of an ideal gas exert **no attractive 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. (image source)
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 *condensed* states of matter (liquids and solids) in which neighboring molecules are constantly in contact. 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.

## 5.2 Kinetic molecular interpretation of gas properties

If gases do in fact consist of widely-separated particles, then the observable properties of gases must be explainable in terms of the simple mechanics that govern the motions of the individual molecules.

**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  $\Delta V$  is equivalent to an *acceleration*  $a$ ; According to Newton's second law, a force  $f = ma$  is thus exerted on the surface of area  $A$  exerting a pressure  $P = f/A$ .



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

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

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 tem-

perature 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.

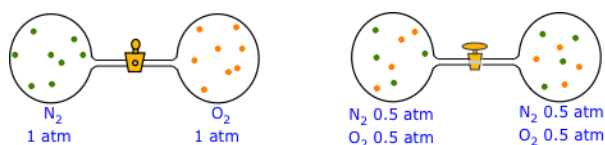
**Kinetic explanation of Boyle's law** Boyle's law is easily explained by the kinetic molecular theory. The pressure of a gas depends on the number of times per second that the molecules strike the surface of the container. If we compress the gas to a smaller volume, the same number of molecules are 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.

### 5.3 Diffusion: random motion with direction

*Diffusion* refers to the transport of matter through a *concentration gradient*; the rule is that substances move (or tend to move) from regions of higher concentration to those of lower concentration. The diffusion of tea out of a teabag into water, or of perfume from a person, are common examples; we would not expect to see either process happening in reverse!

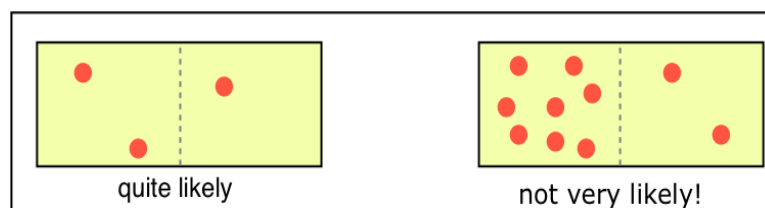


When the stopcock is opened, random motions cause each gas to diffuse into the other container. After diffusion is complete (right), individual molecules of both kinds continue to pass between the flasks in both directions.

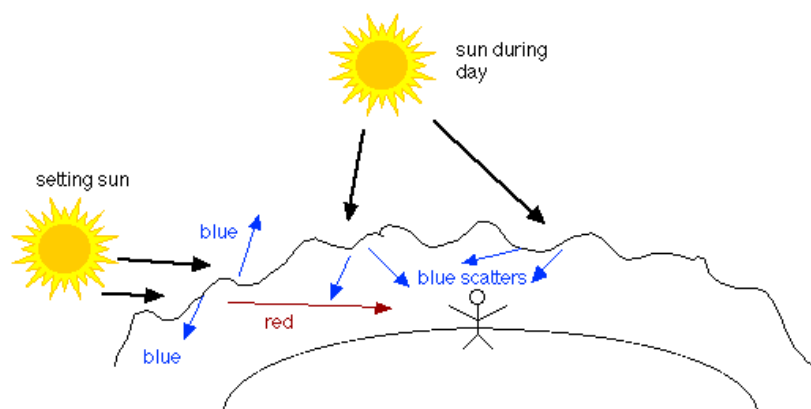
It might at first seem strange that the *random* motions of molecules can lead to a completely predictable drift in their ultimate distribution. The key to this apparent paradox is the distinction between an *individual* and the *population*. Although we can say nothing about the fate of an individual molecule, the behavior of a large collection ("population") of molecules is subject to the laws of statistics. We won't go into the details here, but one simple example should suffice: consider what happens when the stopcock is opened that separates two containers of different gases under identical conditions.

### 5.4 Density fluctuations: Why is the sky blue?

Diffusion ensures that 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.



From <http://www.uccs.edu/~tchrise/>

What we have been discussing is a form of what is known as *fluctuation phenomena*. If a massless partition were inserted into the middle of a container of a gas, the random fluctuations in pressure of a gas on either side would not always completely cancel out, especially when the pressures are quite small. These pressure fluctuations would cause the partition to vibrate.

## 5.5 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,



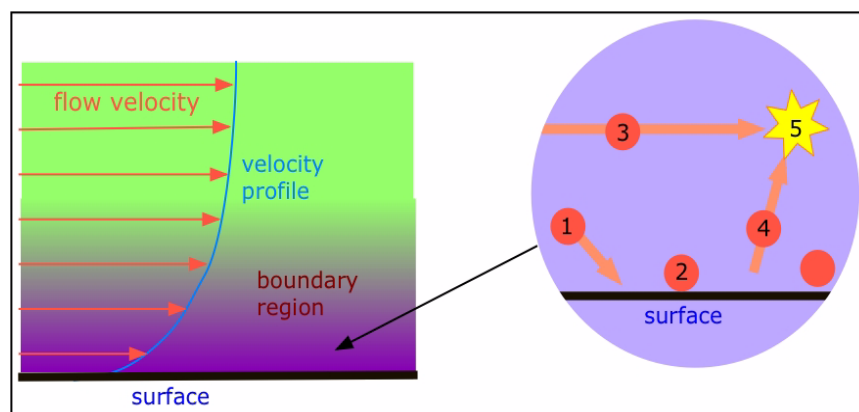
and the bulb would melt. (Thermal conduction depends on intermolecular collisions, and a longer mean free path means a lower collision frequency). A complete vacuum would minimize heat conduction, but this would result in such a long mean free path that the tungsten atoms would rapidly migrate to the 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. The more recently-developed halogen-cycle lamp is an interesting chemistry-based method of prolonging the life of a tungsten-filament lamp.

## 5.6 Viscosity of gases

Gases, like all fluids, exhibit a resistance to flow, a property known as viscosity. The basic cause of viscosity is the random nature of thermally-induced molecular motion. In order to force a fluid through a pipe or tube, an additional non-random translational motion must be superimposed on the thermal motion.

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 lose some of their forward momentum. 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*; this is the reason why long gas transmission pipelines need to have pumping stations every 100 km or so.

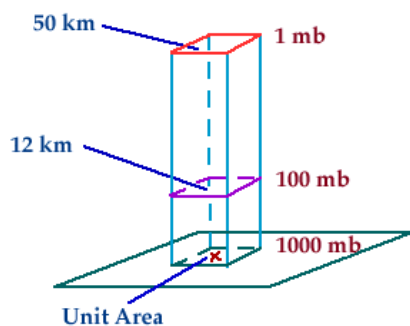


**Origin of gas viscosity in a pipeline.** The magnified view on the right shows the boundary region where random movements of molecules in directions other than the one of the flow (1) move toward the confining surface and temporarily adsorb to it (2). After a short time, thermal energy causes the molecule to be released (4) with most of its velocity not in the flow direction. A rapidly-flowing molecule (3) collides with it (5) and loses some of its flow velocity.

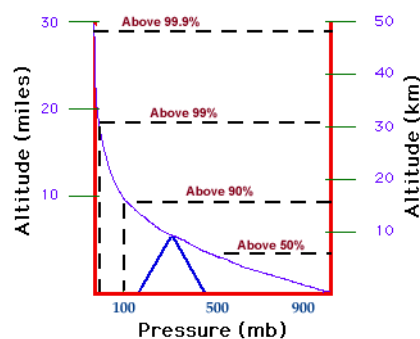
As you know, liquids such as syrup or honey exhibit smaller viscosities at higher temperatures as the increased thermal energy reduces the influence of intermolecular attractions, thus allowing the molecules to slip around each other more easily. Gases, however, behave in just the opposite way; gas viscosity arises from collision-induced transfer of momentum from rapidly-moving molecules to slow ones that have been released from the boundary layer. The higher the temperature, the more rapidly the molecules move and collide with each other, so the higher the viscosity.

## 5.7 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.



The pressure at any elevation in a vertical column of a fluid is due to the weight of the fluid above it. This build-up in the pressure follows an exponential law.

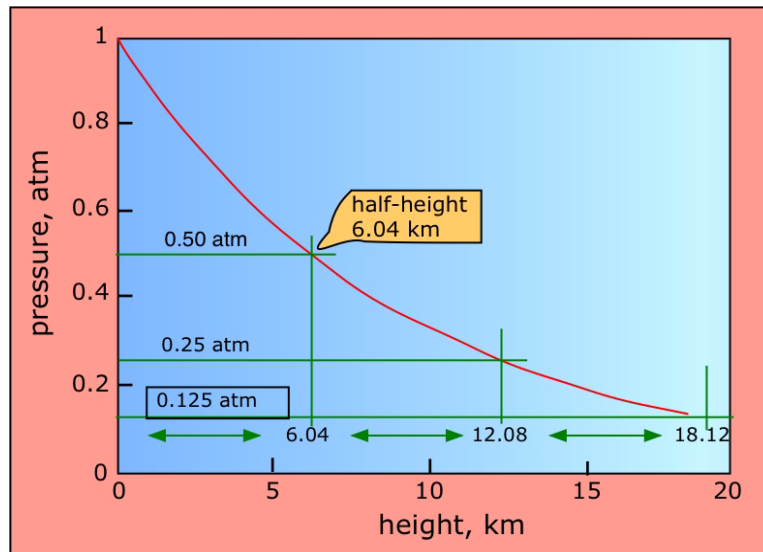


Notice how much more slowly the pressure falls off at higher altitudes; this is because 90 percent of the molecules in the air are below 10 km.

Graphic: [http://ww2010.atmos.uiuc.edu/\(Gh\)/guides/mtr/pw/prs/hght.rxml](http://ww2010.atmos.uiuc.edu/(Gh)/guides/mtr/pw/prs/hght.rxml)

#### Decrease of pressure with altitude for air at 25°C.

Note the constant increment of altitude (6.04 km, the "half height") required to reduce the pressure by half its value. This reflects the special property of an exponential function  $af = fe^y$ , namely that the derivative  $da/dy$  is just  $e^y$  itself.



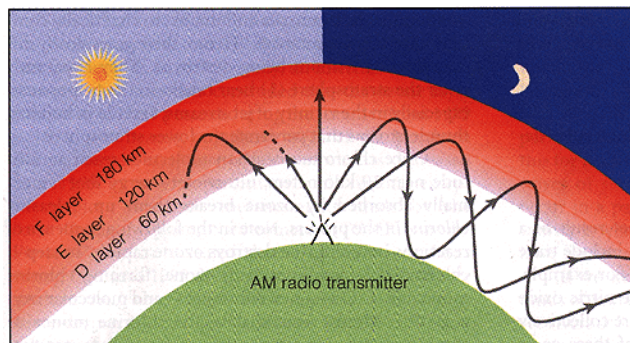
The exact functional relationship between pressure and altitude is known as the *barometric distribution law*. It is easily derived using first-year calculus. For air at 25°C the pressure  $P_h$  at any altitude is given by  $P_h = P_o e^{-.11h}$  in which  $P_o$  is the pressure at sea level. This is 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 6.7 km in the Earth's atmosphere.

Because 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 pressure with altitude. Owing to 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.

## 5.8 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.



<http://apollo.isc.vsc.edu/classes/met130/notes/chapter1/ion2.html>

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.

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## 6 • More on the kinetic-molecular model

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In this section, we look in more detail at some aspects of the kinetic-molecular model and how it relates to our empirical knowledge of gases. For most students, this will be the first application of algebra to the development of a chemical model; this should be educational in itself, and may help bring that subject back to life. As before, your emphasis should be on understanding these models and the ideas behind them, there is no need to memorize any of the formulas.

## 6.1 The velocities of gas molecules

At temperatures above absolute zero, all molecules are in motion. In the case of a gas, this motion consists of straight-line jumps whose lengths are quite great compared to the dimensions of the molecule. Although we can never predict the velocity of a particular individual molecule, the fact that we are usually dealing with a huge number of them allows us to know what fraction of the molecules have kinetic energies (and hence velocities) that lie within any given range.

### Many molecules, many velocities

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 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 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

$$v_{rms} \equiv \sqrt{\frac{\sum v^2}{n}}$$

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:

$$\bar{v} \equiv v_{rms} \equiv \sqrt{\frac{3RT}{m}}$$

in which  $m$  is the molar mass in  $\text{kg mol}^{-1}$ , and  $k = R/6.02 \times 10^{23}$ , the “gas constant per molecule”, is known as the *Boltzmann constant*.

**Problem Example 13**

What is the average velocity of a nitrogen molecules at 300K?

*Solution:* The molar mass of  $N_2$  is 28.01 g. Substituting in the above equation and expressing  $R$  in energy units, we obtain

$$v^2 = \frac{3 \times 8.31 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{28.01 \times 10^{-3} \text{ kg mol}^{-1}} = 2.67 \times 10^5 \text{ J kg}^{-1}$$

Recalling the definition of the joule ( $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$ ) and taking the square root,

$$\bar{v} = \sqrt{2.67 \times 10^5 \text{ J kg}^{-1} \times \frac{1 \text{ kg m}^2 \text{ s}^{-2}}{1 \text{ J}}} = 517 \text{ m s}^{-1}$$

or

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

A simpler formula for estimating average molecular velocities is

$$V = 157 \sqrt{\frac{T}{m}}$$

in which  $V$  is in units of meters/sec,  $T$  is the absolute temperature and  $m$  the molar mass in grams.

Note that the  $N_2$  molecule velocity calculated above is comparable to that of a rifle bullet (typically 300-500  $\text{m s}^{-1}$ .)

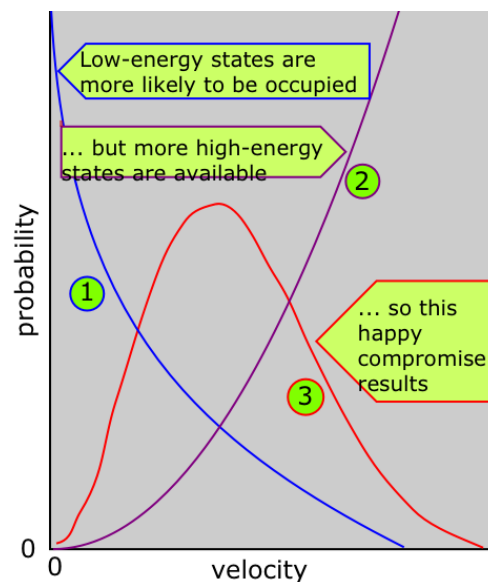
## 6.2 The Boltzmann distribution

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*. This distribution law 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 (1844-1906) put the relation on a sounder theoretical basis and simplified the mathematics somewhat.



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 so many more of these are available (2).

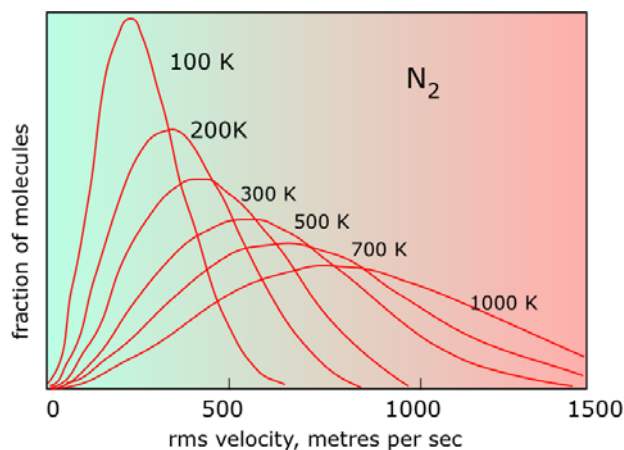


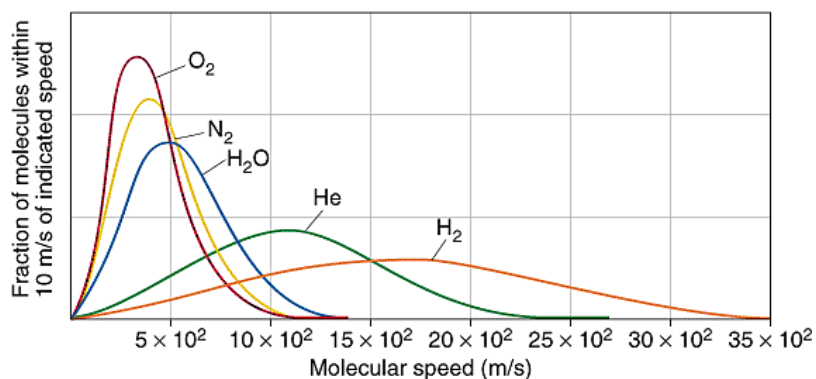
Although the number of possible higher-energy states is greater, the lower-energy states are more likely to be occupied (1). This is because only so much kinetic energy is available to the gas as a whole; every molecule that acquires kinetic energy in a collision leaves behind another molecule having 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 3 seen above. 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.

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.

#### How the temperature affects the distribution of molecular velocities.

Notice how the left ends of the plots are anchored at zero velocity (there will always be a few molecules that happen to be at rest.) As a consequence, the curves flatten out as the higher temperatures make additional higher-velocity states of motion more accessible. The area under each plot is the same for a constant number of molecules.





### How the molecular weight affects the velocity distribution

All molecules have the same kinetic energy ( $mv^2/2$ ) at the same temperature, so the fraction of molecules with higher velocities will increase as the molecular weight decreases.

This plot was taken from a U of Florida Chemistry page which has a good discussion of kinetic-molecular theory, and includes some very nice graphics: [http://itl.chem.ufl.edu/2041\\_f97/lectures/lec\\_d.html](http://itl.chem.ufl.edu/2041_f97/lectures/lec_d.html)

## Boltzmann distribution and planetary atmospheres

The ability of a planet to retain an atmospheric gas depends on the average velocity (and thus on the temperature and mass) of the gas molecules and on the planet's mass, which determines its gravity and thus the escape velocity. In order to retain a gas for the age of the solar system, the average velocity of the gas molecules should not exceed about one-sixth of the escape velocity. The escape velocity from the Earth is 11.2 km/s, and 1/6 of this is about 2 km/s. Examination of the above plot reveals that hydrogen molecules can easily achieve this velocity, and this is the reason that hydrogen, the most abundant element in the universe, is almost absent from Earth's atmosphere.

Although hydrogen is not a significant atmospheric component, water vapor is. A very small amount of this diffuses to the upper part of the atmosphere, where intense solar radiation breaks down the  $H_2O$  into  $H_2$ . Escape of this hydrogen from the upper atmosphere amounts to about  $2.5 \times 10^{10}$  kg/year.

## 6.3 Derivation of the ideal gas equation of state

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.

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 (3)

$$f = ma = m \frac{dv}{dt}$$

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:

$$\text{force per molecule} = f \equiv \frac{d(mv_x)}{dt} = (2mv) \left( \frac{v_x}{2l} \right) = \frac{mv^2}{l} \quad (4)$$

Pressure is force per unit area, so the pressure exerted by the molecule on the wall of cross-section  $l^2$  becomes

$$\text{pressure per molecule} = \frac{mv_x^2}{l^3} = \frac{v_x^2}{V} \quad (5)$$

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 an average value which we will denote by  $\bar{v}^2$ .

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

$$P = \frac{N}{3} \frac{m\bar{v}^2}{V} \quad (6)$$

in which  $V$  is the volume of the container.

Recalling that  $mv^2/2$  is the average translational kinetic energy we can rewrite the above as

$$PV = \frac{1}{3} Nm\bar{v}^2 = \frac{2}{3} N\epsilon \quad (7)$$

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

$$f = ma = m \frac{dv}{dt} \quad (8)$$

in which the proportionality constant  $k$  is known as the *Boltzmann constant*. For one mole of molecules we express this proportionality constant as  $(6.02E23)k = R$  in which is  $R$  is the familiar *gas constant*.

Substituting into (8) yields the *ideal gas equation*

$$PV = RT$$

Since the product  $PV$  has the dimensions of energy, so does  $RT$ , and this quantity in fact represents the average translational kinetic energy per mole. The relationship between these two energy units can be obtained by recalling that  $1\text{ atm}$  is  $1.013E5\text{ N m}^{-2}$ , so that

*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:

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

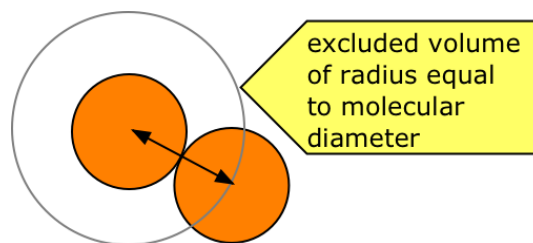
Notice that the Boltzmann constant  $k$ , which appears in many expressions relating to the statistical treatment of molecules, is just  $R/6.02E23$ , the "gas constant per molecule."

#### 6.4 How far does a molecule travel between collisions?

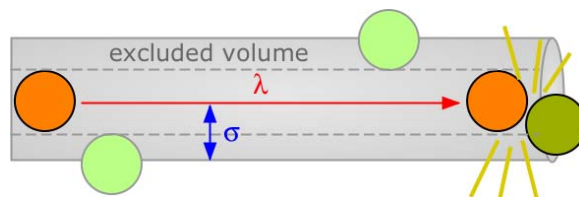
Molecular velocities tend to be very high by our everyday standards (typically around  $500\text{ metres per sec}$ ), but even in gases, they bump into each other so frequently that their paths are continually being deflected in a random manner, so that the net movement (*diffusion*) of a molecule from one location to another occurs rather slowly.

##### How close can two molecules get?

Each molecule is surrounded by an imaginary sphere (gray circle) whose radius  $\sigma$  is equal to the sum of the radii of the colliding molecules. This sphere defines the excluded volume, within which the center of another molecule cannot enter.



The average distance a molecule moves between such collisions is called the *mean free path*. This distance, denoted by  $\lambda$  (*lambda*), depends on the number of molecules per unit volume and on their size. To avoid collision, a molecule of diameter  $\sigma$  must trace out a path corresponding to the axis of an imaginary cylinder whose cross-section is  $\pi\sigma^2$ . Eventually it will encounter another molecule (extreme right in the diagram below) that has intruded into this cylinder and defines the terminus of its free motion.



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  $\lambda n \pi \sigma^2$ . Solving for  $\lambda$  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

(9)

$$\lambda = \frac{1}{\sqrt{2} n \pi \sigma^2}$$

Small molecules such as He, H<sub>2</sub> and CH<sub>4</sub> typically have diameters of around 30-50 nm. At STP the value of  $n$ , the number of molecules per cubic metre, is

(10)

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

Substitution into (10) yields a value of around  $10^{-7}$  m (100 nm) for the mean free path of 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.

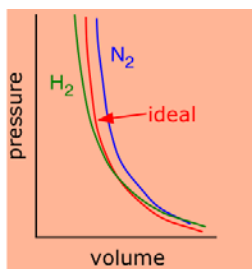
On the other hand, at each collision the molecule can be expected to change direction. Because these changes are random, the net change in location a molecule experiences during a period of one second is typically rather small. Thus in spite of the high molecular velocities, the speed of molecular *diffusion*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

## 7 • Real gases

The "ideal gas laws" as we know them do a remarkably good job of describing the behavior of a huge number chemically diverse substances as they exist in the gaseous state under ordinary environmental conditions, roughly around 1 atm pressure and a temperature of 300 K. This is especially so when we consider that some of the basic tenets of the ideal gas model have to be abandoned in order to explain such properties as

- the average distance between collisions (the molecules really do take up space)
- the viscosity of a gas flowing through a pipe (the molecules do get temporarily "stuck" on the pipe surface, and are therefore affected by intermolecular attractive forces.)

Even so, many of the common laws such as Boyle's and Charles' continue to describe these gases quite well even under conditions where these phenomena are evident.

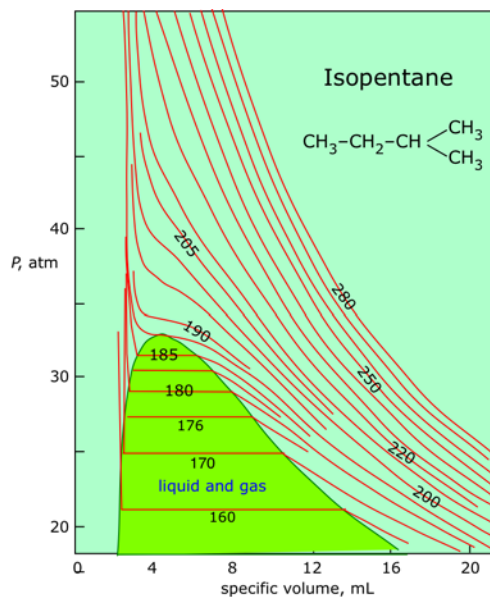


Under ordinary environmental conditions (moderate pressures and above 0°C), the isotherms of substances we normally think of as gases don't appear to differ very greatly from the hyperbolic form

$$(PV/RT) = \text{constant.}$$

... but over a wider range of conditions, things begin to get more complicated. Thus Isopentane, shown here, behaves in a reasonably ideal manner above 210 K, but below this temperature the isotherms become somewhat distorted, and at 185K and below they cease to be continuous, showing peculiar horizontal segments in which reducing the volume does not change the pressure.

It turns out that real gases eventually begin to follow their own unique equations of state, and ultimately even cease to be gases. In this unit we will see why this occurs, what the consequences are, and how we might modify the ideal gas equation of state to extend its usefulness over a greater range of temperatures and pressures.



## 7.1 Effects of intermolecular forces

According to Boyle's law, the product  $PV$  is a constant at any given temperature, so 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 as the molecules are crowded closer together. But we know that the molecules themselves are finite objects having volumes of their own, and this must place a lower limit on the volume into which they can be squeezed. So we must reformulate the ideal gas equation of state as a relation that is true only in the *limiting case of zero pressure*:

$$\lim_{P \rightarrow 0} PV = nRT$$

So what happens when a real gas is subjected to a very high pressure? The outcome varies with both the molar mass of the gas and its temperature, but in general we can see the effects of both repulsive and attractive intermolecular forces:

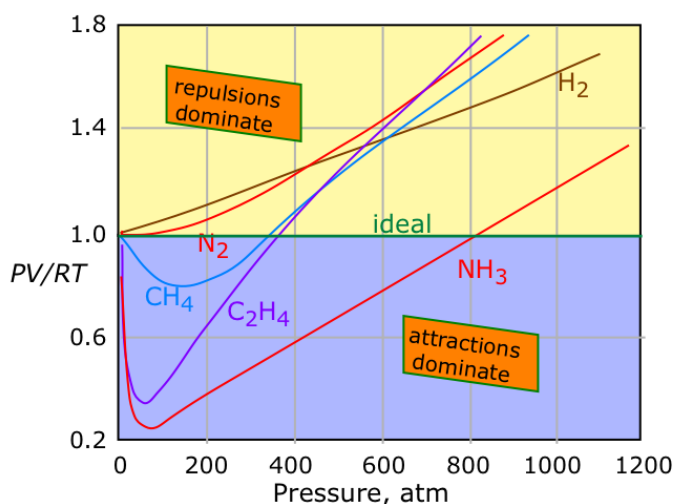
**Repulsive forces:** As a gas is compressed, the individual molecules begin to get in each other's way, giving rise to a very strong *repulsive force* acts to oppose any further volume decrease. We would therefore expect the  $PV$  vs  $P$  line to curve upward at high pressures, and this is in fact what is observed for all gases at sufficiently high pressures.

**Attractive forces:** 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*.

A plot of  $PV/RT$  as a function of pressure is a very sensitive indicator of deviations from ideal behavior, since such a plot is just a horizontal line for an ideal gas. The two illustrations below show how these plots vary with the nature of the gas, and with temperature.



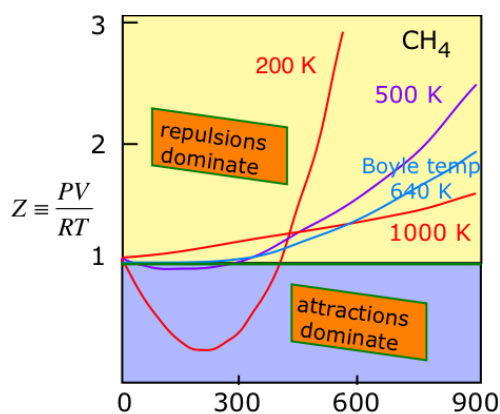
### Effects of intermolecular attractions

Intermolecular attractions, which generally increase with molecular weight, cause the  $PV$  product to decrease as higher pressures bring the molecules closer together and thus within the range of these attractive forces; the effect is to cause the volume to decrease more rapidly than it otherwise would. But as the molecules begin to intrude on each others' territory, repulsive forces always eventually win out.

### Temperature reduces the effects of intermolecular attractions

At higher temperatures, increased thermal motions overcome the effects of intermolecular attractions which normally dominate at lower pressures. So all gases behave more ideally at higher temperatures.

For any gas, there is a special temperature (the *Boyle temperature*) at which attractive and repulsive forces exactly balance each other at zero pressure. As you can see in this plot for methane, this balance does remain as the pressure is increased.

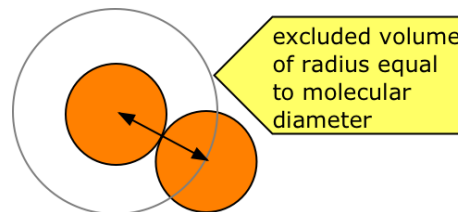


The effect of intermolecular attractions on a  $PV$ -vs.- $P$  plot would be to hold the molecules slightly closer together, so that the volume would decrease more rapidly than the pressure increases. The resulting curve would dip downward as the pressure increases, and this dip would be greater at lower 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.

## 7.2 Equations of state for real gases: the van der Waals equation

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 (1837-1923) 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  $(V - b)$  which is known as the *excluded volume*, typically of the order of  $20\text{--}100\text{ cm}^3\text{ mol}^{-1}$ . The excluded volume (indicated by the gray circle at the right) surrounding any molecule defines the closest possible approach of any two molecules during collision.



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 constants  $a$  and  $b$  depend respectively on the magnitudes of the attractive and repulsive forces in a particular gas. The complete van der Waals equation of state thus becomes

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

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.

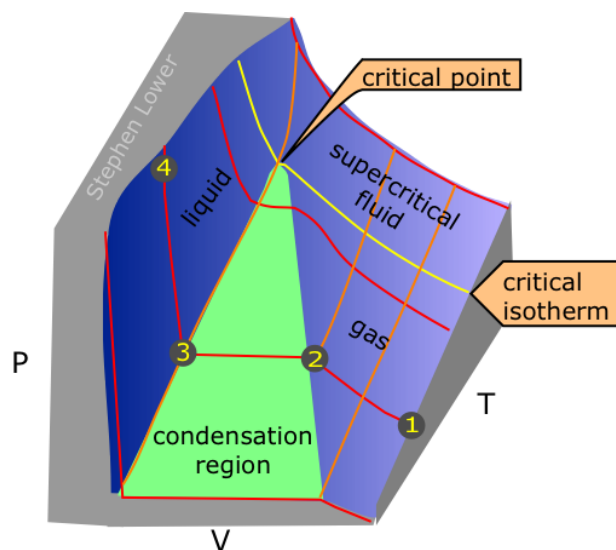
substance	molar mass/g	a (L <sup>2</sup> -atm mol <sup>-2</sup> )	b (L mol <sup>-1</sup> )
hydrogen H <sub>2</sub>	2	0.244	0.0266
helium He	4	0.034	0.0237
methane CH <sub>4</sub>	16	2.25	0.0428
water H <sub>2</sub> O	18	5.46	0.0305
nitrogen N <sub>2</sub>	28	1.39	0.0391
carbon dioxide CO <sub>2</sub>	44	3.59	0.0427
carbon tetrachloride CCl <sub>4</sub>	110	20.4	0.1383

**Table 1: van der Waals constants for some gases**

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 chemical engineering work in which the behavior of gases at high pressures must be accurately predicted.

### 7.3 Condensation and the critical point

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 plot below illustrates 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, *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.



### PVT surface of a real gas

To better understand this plot, look at the isotherm labeled 1. As the gas is compressed from 1 to 2, the pressure rises in much the same way as Boyle's law predicts. Compression beyond 2, however, does not cause any rise in the pressure. What happens instead is that some of the gas condenses to a liquid. At 3, the substance is entirely in its liquid state. The very steep rise to 4 corresponds to our ordinary experience that liquids have very low compressibilities. The range of volumes possible for the liquid (indicated by the width of the green wedge-shaped cross section) diminishes as the critical temperature is approached.

gas	$P_c$ , atm	$V_c$ , $\text{cm}^3 \text{mol}^{-1}$	$T_c$ , K
He	2.3	58	5.2
Ne	27	42	44
Ar	48	75	150
Xe	58	119	290
H <sub>2</sub>	13	65	33
O <sub>2</sub>	50	78	155
N <sub>2</sub>	34	90	126
CO <sub>2</sub>	73	94	302
H <sub>2</sub> O	73	94	302
NH <sub>3</sub>	111	72	405
CH <sub>4</sub>	46	99	191

### Critical constants of some gases

Note especially

- The very low critical pressure and temperature of **helium**, reflecting the very small intermolecular attractions of this atom.
- $T_c$  of the **noble gas elements** increases with atomic number
- **Hydrogen** gas cannot be liquified above 33 K; this poses a major difficulty in the use of hydrogen as an automotive fuel; storage as a high-pressure gas requires heavy steel containers which add greatly to its effective weight-per-joule of energy storage.
- The properties of **carbon dioxide** (particularly its use as a supercritical fluid) are described above.
- The high  $T_c$  of **water** is another manifestation of its "anomalous" properties relating to hydrogen-bonding.

## Supercritical fluids

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



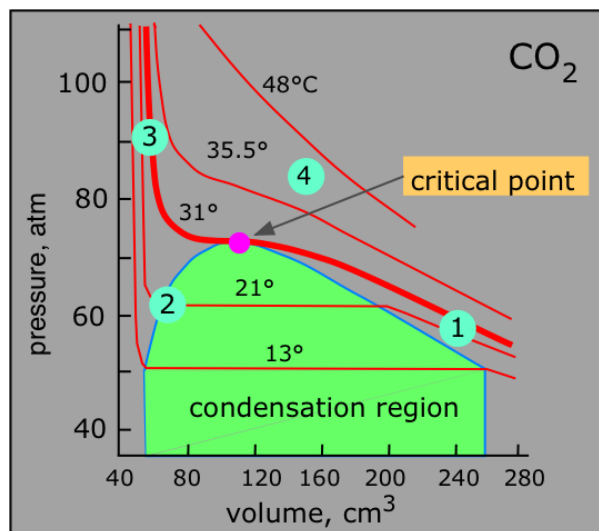
and gas can coexist only within the regions indicated by the wedge-shaped cross section on the left and the shaded area in the diagram above. An important consequence of this is that *a liquid phase cannot exist at temperatures above the critical point.*

The critical point of a gas is defined by its critical temperature, pressure and volume, denoted by  $T_c$ ,  $P_c$ , and  $V_c$ .

The critical temperature of carbon dioxide is  $31^\circ\text{C}$ , so you can tell whether the temperature is higher or lower than this by shaking a  $\text{CO}_2$  fire extinguisher; on a warm day, you will not hear any liquid sloshing around inside. The critical temperature of water is  $374\text{K}$ , and that of hydrogen is only  $33\text{K}$ .

#### Critical behavior of carbon dioxide

At temperatures below  $31^\circ\text{C}$  (the critical temperature),  $\text{CO}_2$  acts somewhat like an ideal gas at higher pressures (1). Below this temperature, subjecting the gas to a higher pressure eventually causes condensation to begin. Thus at  $21^\circ\text{C}$ , at a pressure of about  $62\text{atm}$ , the volume can be reduced from  $200\text{cm}^3$  to about  $55\text{cm}^3$  without any further rise in the pressure. Instead of the gas being compressed, it is replaced with the far more compact liquid as the gas is essentially being "squeezed" into its liquid phase. After all of the gas has disappeared (2), the pressure rises very rapidly because now all that remains is an almost incompressible liquid. The isotherm 3 that passes through the critical point is called the critical isotherm. Above this isotherm (4),  $\text{CO}_2$  exists only as a *supercritical fluid*.



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!

#### Supercritical fluids

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. The density of a supercritical fluid can be changed over a wide range by adjusting the pressure; this, in turn, changes its solubility, which can thus be optimized for a particular application. The picture at the right shows a commercial laboratory device used for carrying out chemical reactions under supercritical conditions.

**Supercritical carbon dioxide** is widely used to dissolve the caffeine out of coffee beans and as a dry-cleaning solvent. **Supercritical water** has recently attracted interest as a medium for chemically decomposing dangerous environmental pollutants such as PCBs.