

UNDERSTANDING PRESSURE

Pressure Calculations

The mass of the atmosphere is 5.136×10^{18} kg. The surface area of the earth is 5.101×10^{14} m². Calculate atmospheric pressure.

$$P = F/\text{Area}$$

$$F = mg = 5.136 \times 10^{18} \text{ kg} \times 9.8 \text{ m s}^{-2} = 5.0 \times 10^{19} \text{ N m}^{-2}$$

$$P = 5.0 \times 10^{19} \text{ N m}^{-2} / 5.101 \times 10^{14} \text{ m}^2 = 9.8 \times 10^4 \text{ Pa}$$



UNDERSTANDING PRESSURE

Pressure Calculations

Airplanes stay aloft due to the upward force on the wings from the difference in air pressure below and above the wings. For a 450,000 lb airplane with a wing area of 7,000 ft², what does this pressure difference have to be to keep the plane aloft?

Force of the pressure difference between the top and bottom of the wings must offset gravitational force on plane. $450,000 \text{ lb} / (7,000 \text{ ft}^2 \times 144 \text{ in}^2 \text{ ft}^{-2}) = 0.5 \text{ lb in}^{-2}$, i. e. 0.5 psi.



UNDERSTANDING PRESSURE

Pressure Calculations



PROPERTIES OF PHASES

Compressibility Calculations

Changes in atmospheric pressure associated with low pressure and high pressure air masses are of the order of 0.02 atm. For a pressure increase from 0.99 to 1.01 atm calculate the fractional change in volume for water as a solid, liquid, and gas.

$\kappa = -(\delta V/V)/\delta P$, so $\delta V/V = -\kappa \delta P$ and $\delta P = 0.02$ atm, so:

$$\delta V/V = -1.1 \times 10^{-6} \text{ H}_2\text{O}(s)$$

$$\delta V/V = -9.0 \times 10^{-7} \text{ H}_2\text{O}(l)$$

$$\delta V/V = -0.02 \text{ H}_2\text{O}(g)$$



PROPERTIES OF PHASES

Compressibility Calculations

The pressure at the top of Mt. Everest is 0.320 atm. Using compressibility data, estimate the change in density in taking a sample of ice from sea level to the top of Mt. Everest.

$\kappa = -(\delta V/V)/\delta P$, so $\delta V/V = -\kappa \delta P$ and $\delta P = 0.680$ atm, so:
 $\delta V/V = -3.6 \times 10^{-5}$. Now, $d = m/V$ or $d \times V = m =$
constant.

So $(d + \delta d)(V + \delta V) = \text{constant} = d \times V$.

and $[(d + \delta d)(V + \delta V)]/(d \times V) = 1$

$$[(1 + \delta d/d)] [(1 + \delta V/V)] = 1$$

$$[(1 + \delta d/d)] [(1 - 3.6 \times 10^{-5})] = 1$$

$$\delta d/d = +3.6 \times 10^{-5}$$



PROPERTIES OF PHASES

Thermal Expansivity Calculations

The thermal expansivity of mercury is 0.000133 K^{-1} . If 0.00330 cm^3 of mercury is contained in a tube of diameter 0.00450 cm how much will the height of the mercury in the tube increase for a temperature rise of 17 K ? (Note: You must assume that the tube itself does not expand.)

$\alpha = (\delta V/V)/\delta T$, so $\delta V/V = \alpha \delta T$ and $\delta T = 17 \text{ K}$, so:
 $\delta V/V = 2.26 \times 10^{-3}$ and $\delta V = 7.46 \times 10^{-6} \text{ cm}^3$. Now,
 $\delta V = (\pi r^2)\delta l$ and $r = 2.25 \times 10^{-3} \text{ cm}$ so $\delta l = 0.469 \text{ cm}$.



UNDERSTANDING DENSITY

Measurements on water show a molecular volume of $1.7 \times 10^{-23} \text{ cm}^3 \text{ molecule}^{-1}$.

The molecular density is $1/(1.7 \times 10^{-23} \text{ cm}^3 \text{ molecule}^{-1}) = 5.9 \times 10^{22} \text{ molecule cm}^{-3}$.

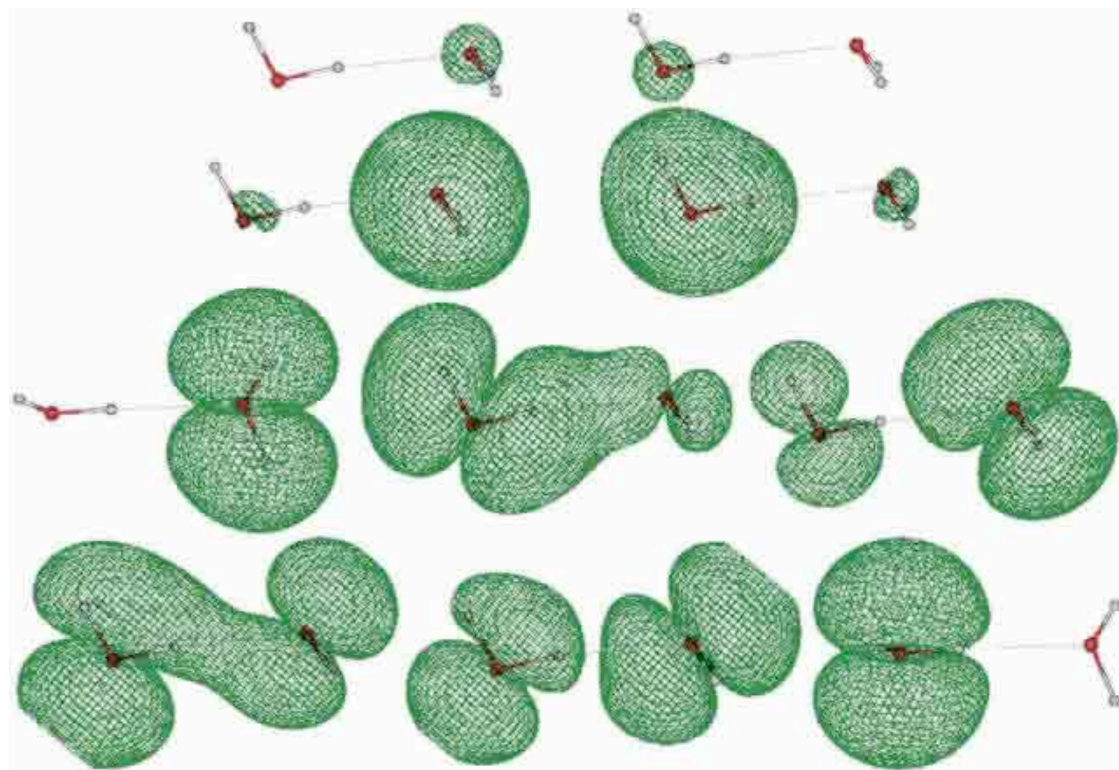
The mass density, d , implied by this molecular density is
 $d = (18.0 \text{ g mole}^{-1}/6.022 \times 10^{23} \text{ molecules mole}^{-1})$
 $\quad \times 5.9 \times 10^{22} \text{ molecule cm}^{-3}$
 $= 1.8 \text{ g cm}^{-3}$

The density is very close to the actual density of liquid and solid water, $d = 1.0 \text{ g cm}^{-3}$.



UNDERSTANDING DENSITY

Packing of Water Molecules



The actual density cannot be quite as high as the result of our calculation, which assumes the water molecules can be packed to occupy all space.



UNDERSTANDING DENSITY

Density Calculations

Calculate the densities of Li(s), Na(s), K(s), Rb(s), and Cs(s) based on their atomic radii. Compare the result to actual densities (tabulated in the Handbook of Chemistry and Physics available on-line in our library).

Answer in next lecture.



UNDERSTANDING DENSITY

Molecules in solids and liquids are packed together about as closely as their size allows.

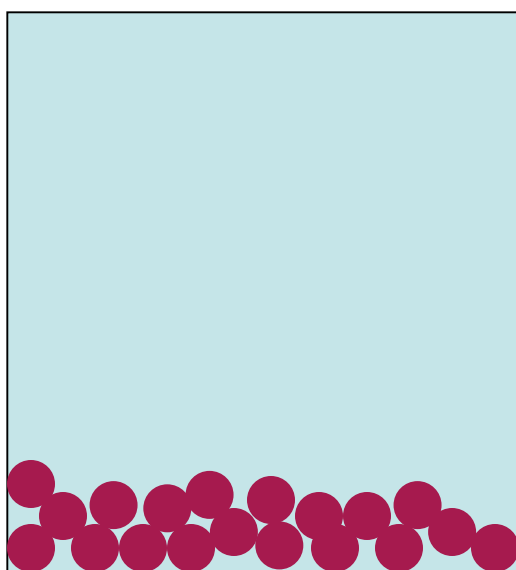
The density of a gas at 1 atm pressure is only about 0.001 times the density of the same substance as a liquid or solid.

Conclusion: In a gas most of the volume occupied by the gas is actually empty space.

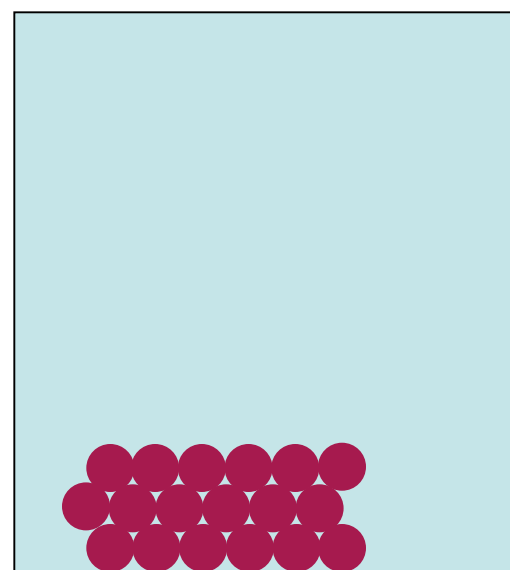
Yet a property of all gases is that they expand to occupy all of the container in which they are placed.



A MOLECULAR VIEW



Liquid



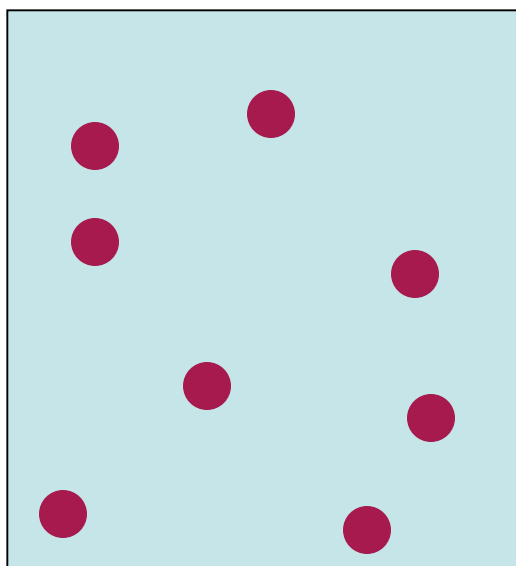
Solid

Density limited by molecular size.

Compressibility low due to close packing.



A MOLECULAR VIEW



Density low due to large spacing between molecules.

Compressibility high due to large spacing between molecules.

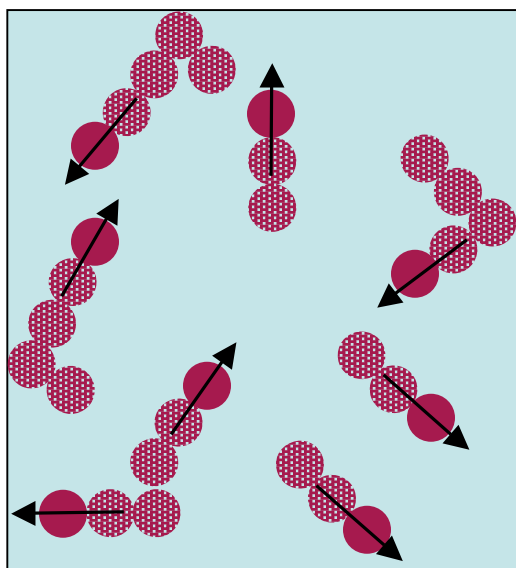
Gas

Why does the gas exert a pressure on the walls?

Why don't the molecules fall to the bottom?



MOLECULES IN MOTION



Gas

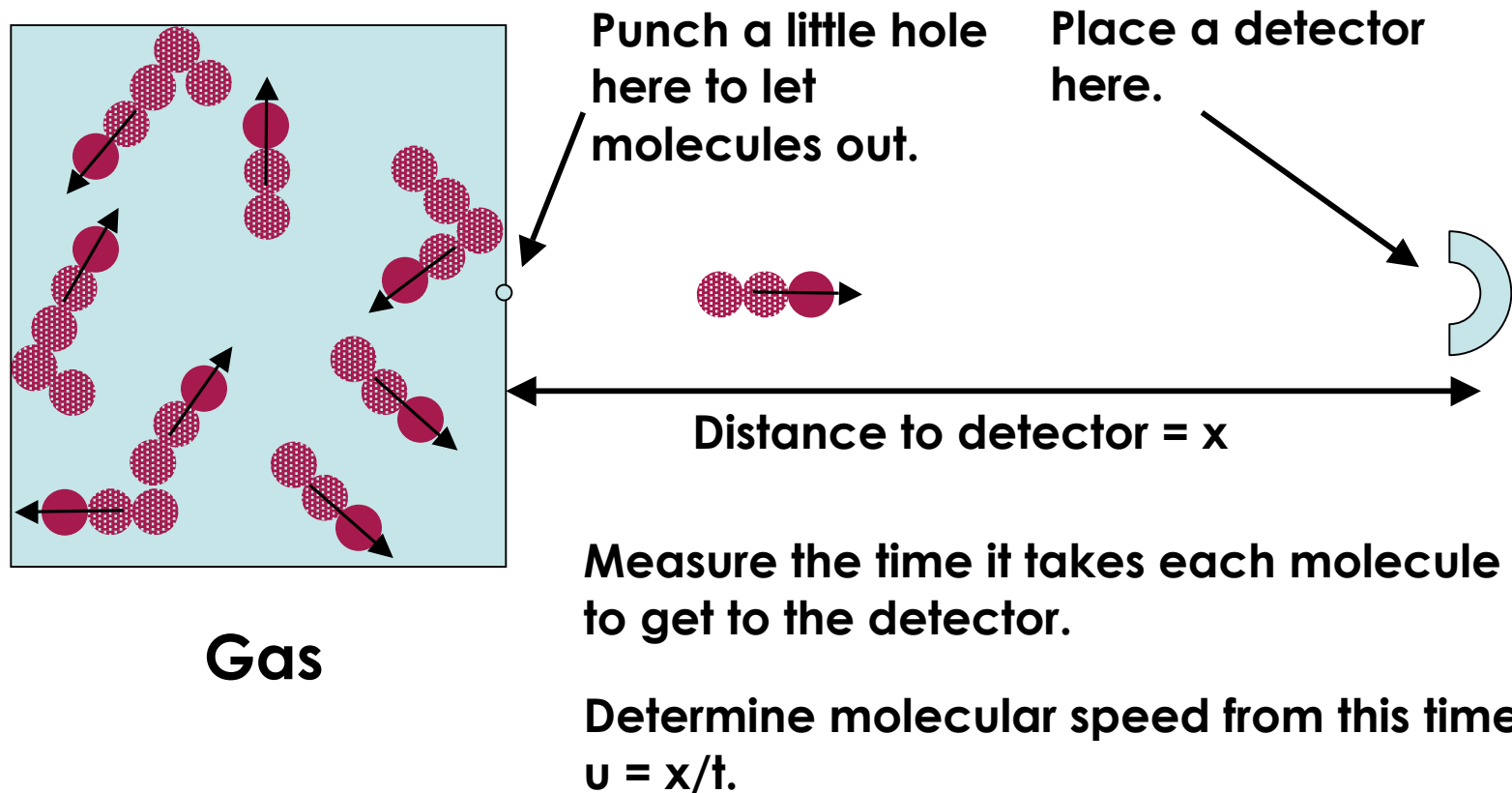
The molecules are in constant random motion.

The speeds of the molecules are determined by the temperature.

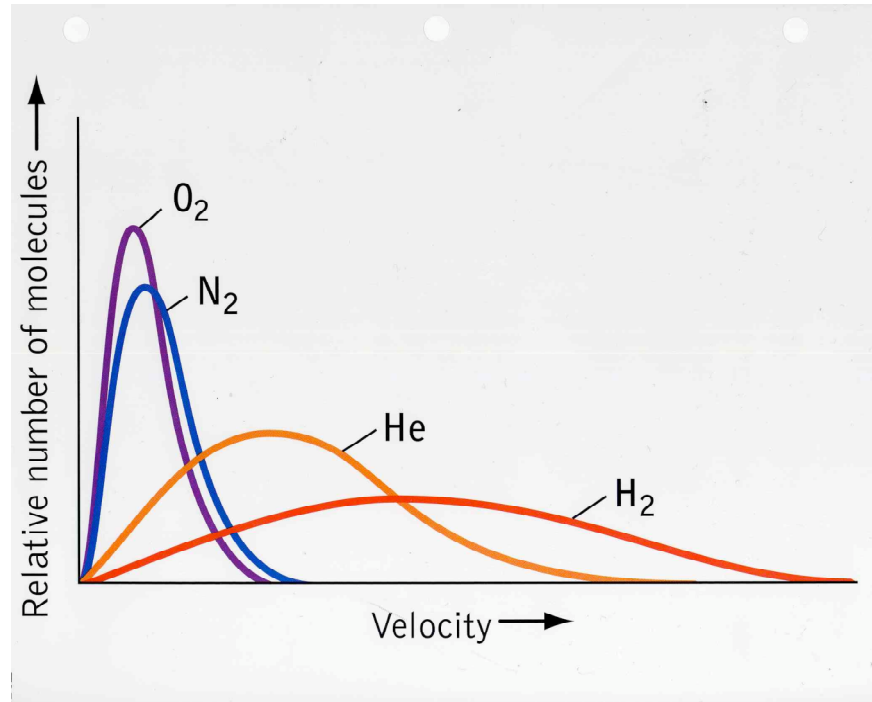
Impact of collisions with the walls gives rise to the pressure.



MOLECULAR VELOCITY DETERMINATION



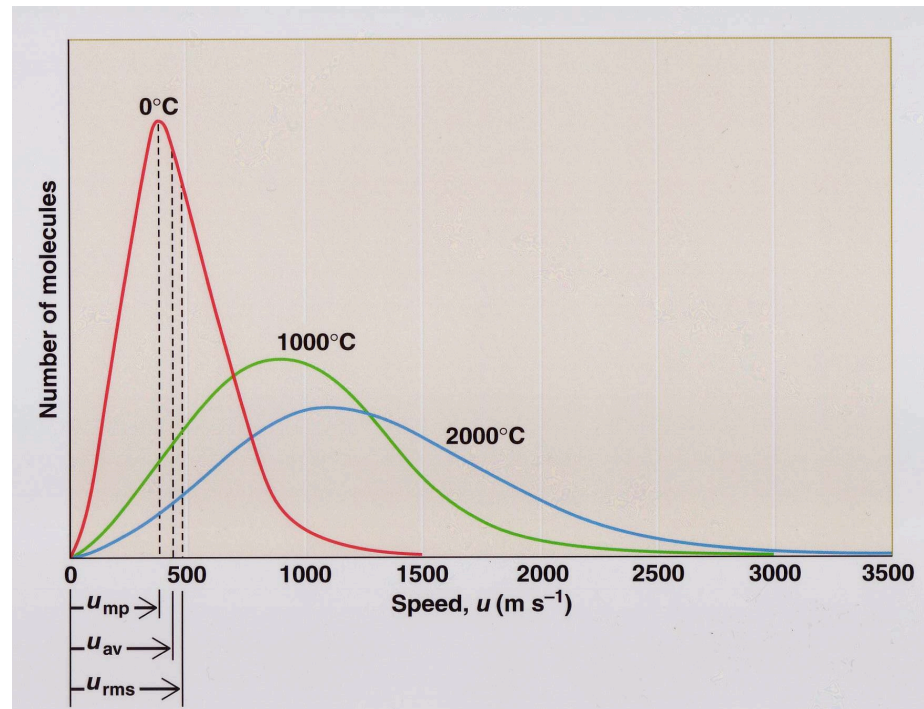
MOLECULAR VELOCITY DETERMINATION



The molecules have a distribution of velocities.
The velocity distribution depends on the mass.



MOLECULAR VELOCITY DETERMINATION

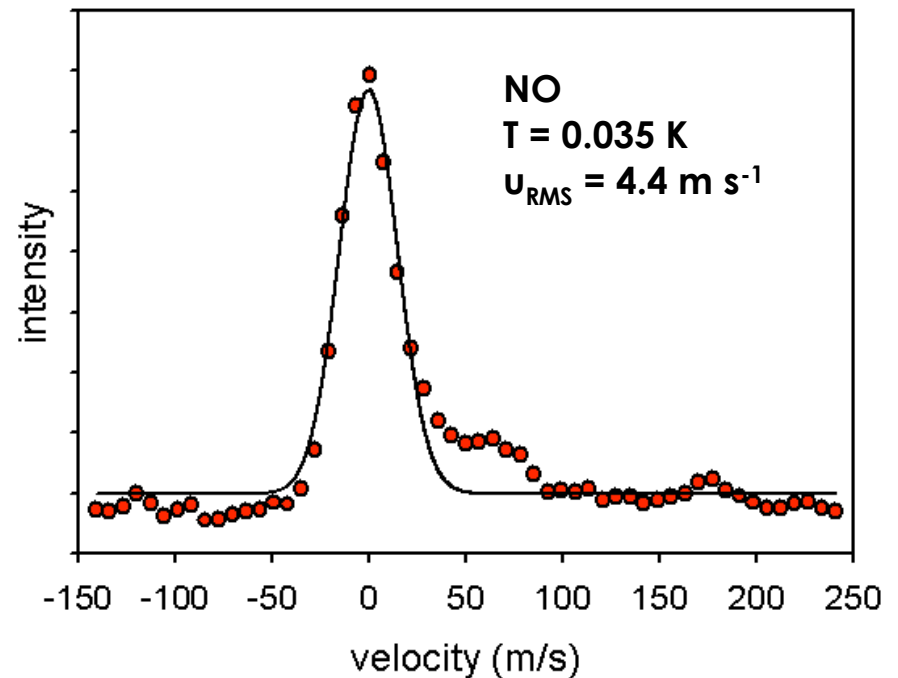
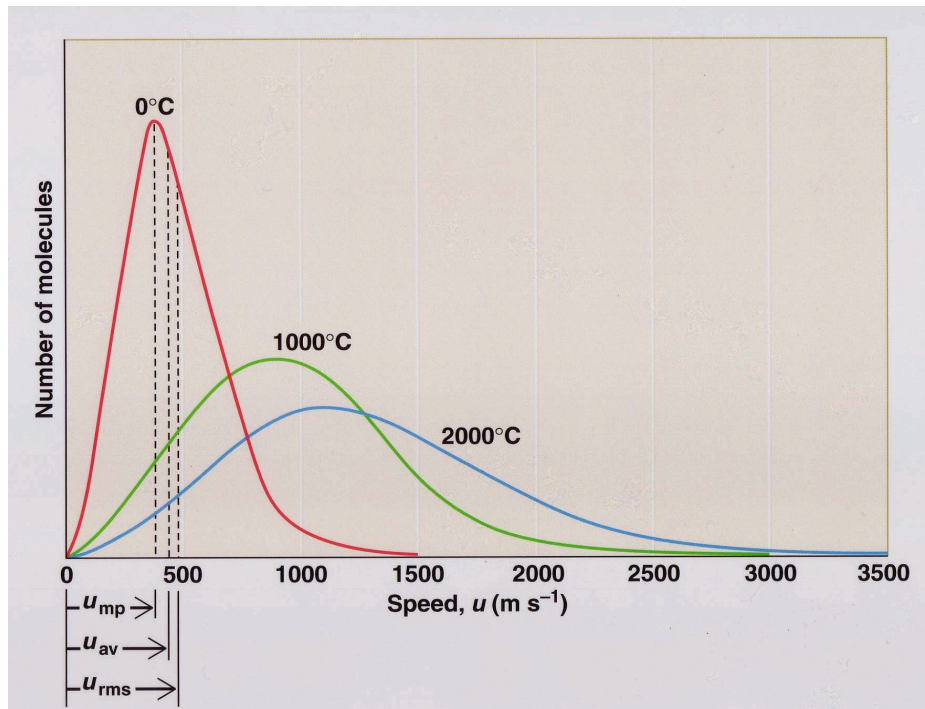


The molecules have a distribution of velocities.

The velocity distribution depends on the temperature.



MOLECULAR VELOCITY DETERMINATION

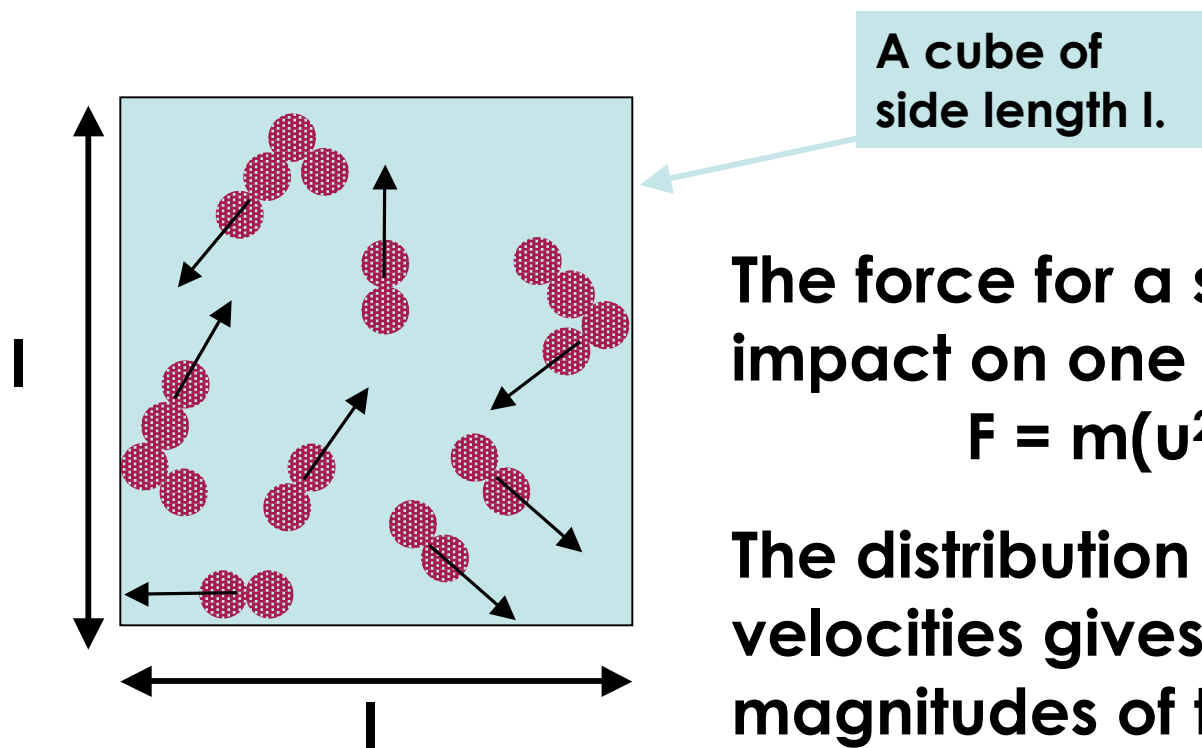


The velocity distribution depends on the temperature.



MOLECULAR BASIS OF PRESSURE

The pressure (Force/Area) is the result of the collection of individual molecular impacts on the walls of the container.



The force for a single molecular impact on one wall is:

$$F = m(u^2/3)/l.$$

The distribution of molecular velocities gives a distribution of magnitudes of this force.



MOLECULAR BASIS OF PRESSURE

The average force for all the N molecules on one wall is:

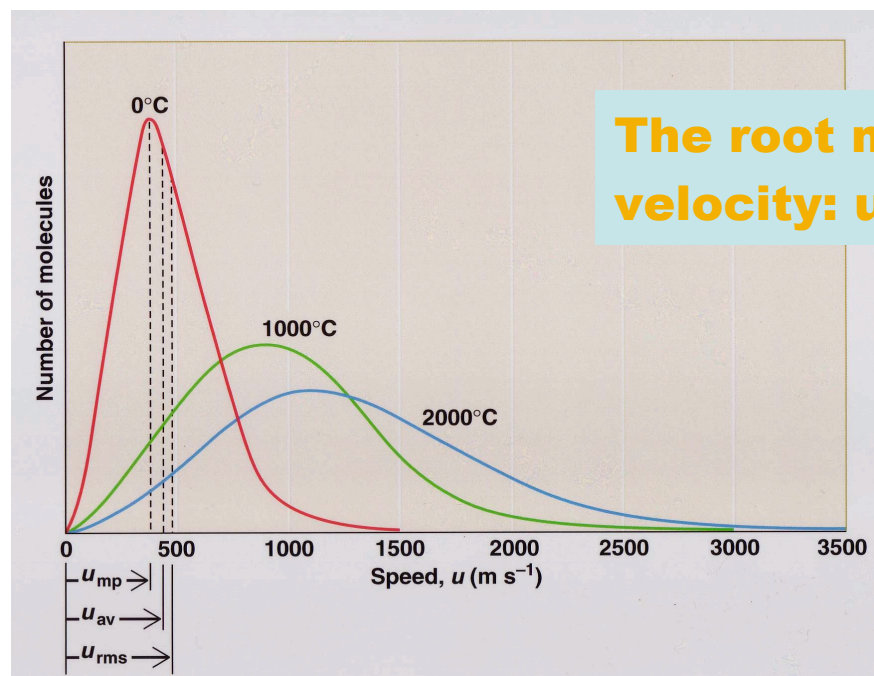
$$\langle F \rangle = N \langle m(u^2/3) / l \rangle$$

— means the average, also.

$$= N(m/3l) \langle u^2 \rangle$$

$$= N(m/3l) \overline{u^2} \quad \leftarrow \text{The mean square velocity.}$$

$\langle \rangle$ means the average.



The root mean square velocity: $u_{\text{rms}} = (\overline{u^2})^{1/2}$.



MOLECULAR BASIS OF PRESSURE

The average force for all the N molecules on one wall is:

$$\langle F \rangle = Nm / (3l) \overline{u^2}.$$

The pressure is this force divided by the area of one face of the cube:

$$\begin{aligned} P &= \langle F \rangle / A = \langle F \rangle / l^2 \\ &= Nm / (3l^3) \overline{u^2} = Nm / (3l^3) \overline{u^2} = Nm / (3V) \overline{u^2}. \end{aligned}$$

The mean square velocity is $\overline{u^2} = 3kT/m$.

Boltzmann Constant
 $k = 1.308630 \times 10^{-23} \text{ J K}^{-1}$

Temperature on the
Kelvin Scale



MOLECULAR BASIS OF PRESSURE

So:

$$P = NkT/V = nN_0kT/V = nRT/V.$$

Number of moles

Avogadro's Number

$$N_0 = 6.02214 \times 10^{23} \text{ mol}^{-1}$$

Universal Gas Constant

$$R = 8.31447 \text{ J mol}^{-1} \text{ K}^{-1}$$

The Ideal Gas Law: $PV = nRT$.



THE IDEAL GAS LAW

The Ideal Gas Law

$$PV = nRT$$

This is called the Ideal Gas Law because the analysis that leads to it assumes that the molecules do not interact with one another. All real molecules do interact.

However, experiments show that the Ideal Gas Law is a pretty good description of real gases under most conditions.

There are simple ways to modify the Ideal Gas Law to get a relation between P, V, and T that is a quantitatively good description of real gases.



THE EQUATION OF STATE

The Ideal Gas Law is an **Equation of State**.

An Equation of State is a mathematical formula that relates the variables P , V , and T .

We can write $P = nRT/V$ or $V = nRT/P$ or $T = PV/nR$. All are Equations of State for the Ideal Gas.

The Equation of State is important. Everything that can be said, everything that can be known, about the gas is specified by a particular combination of P , V , and T .

This is true for any Equation of State, for any gas, liquid, or solid.



EQUATIONS OF STATE

For liquids and solids there is an Equation of State specific to a particular substance.

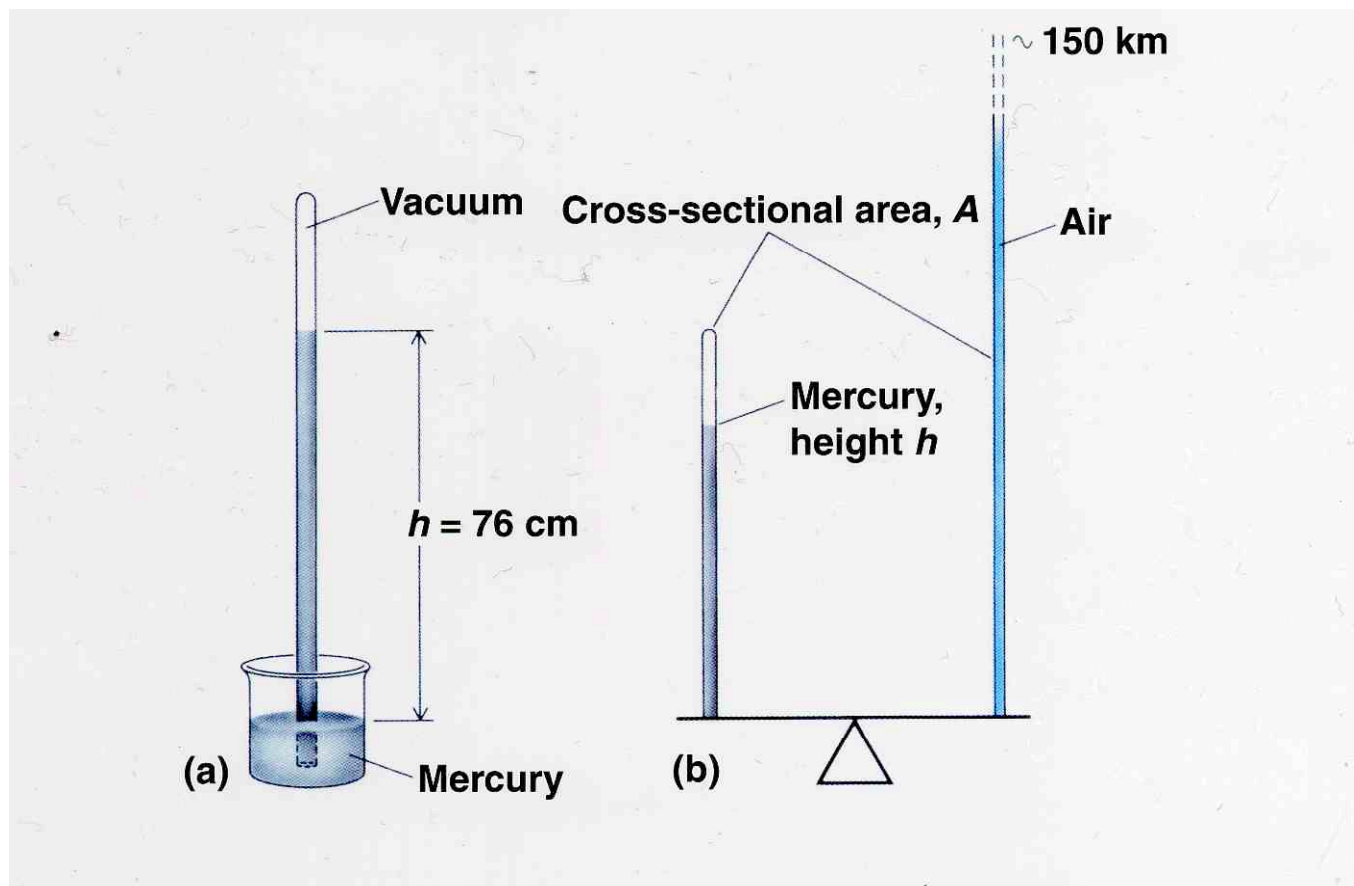
There is no general Equation of State for liquids or solids.

However, the Ideal Gas Law is entirely general. It does not make reference to any characteristic of any particular substance.

The Ideal Gas Law actually was first developed by generalizing experimental observations using real gases.



MEASURING PRESSURE

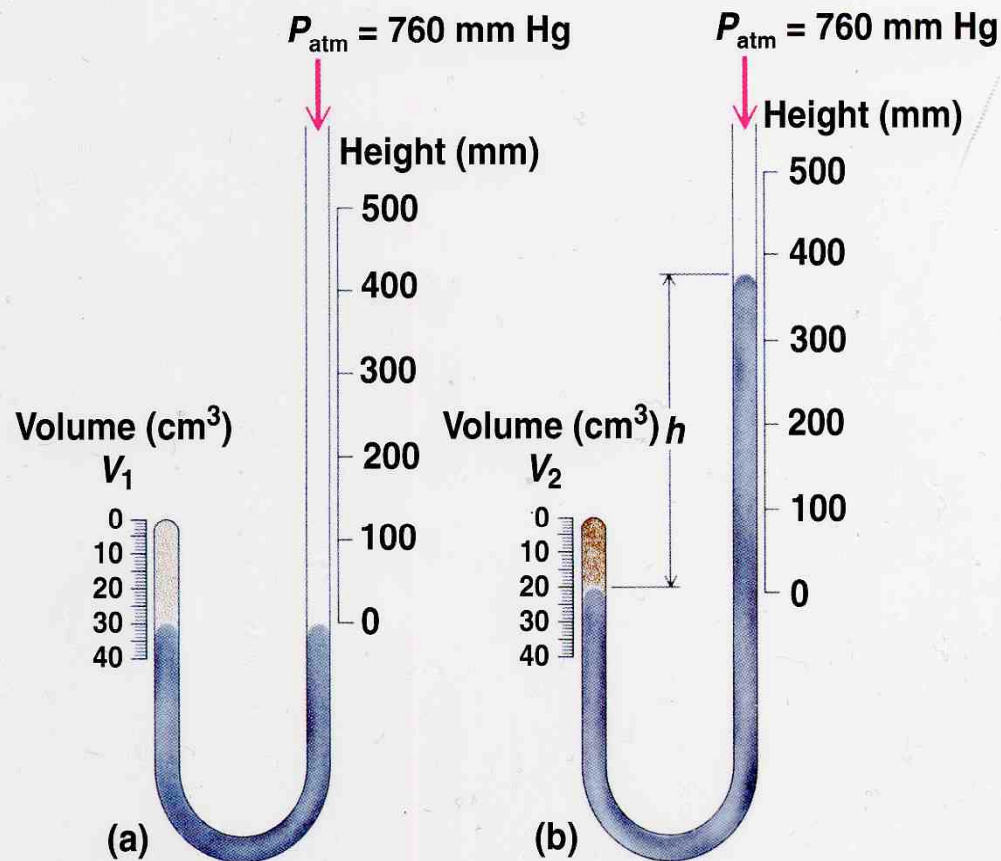


DETERMINING PV BEHAVIOR



Robert Boyle

Boyle's J-Tube

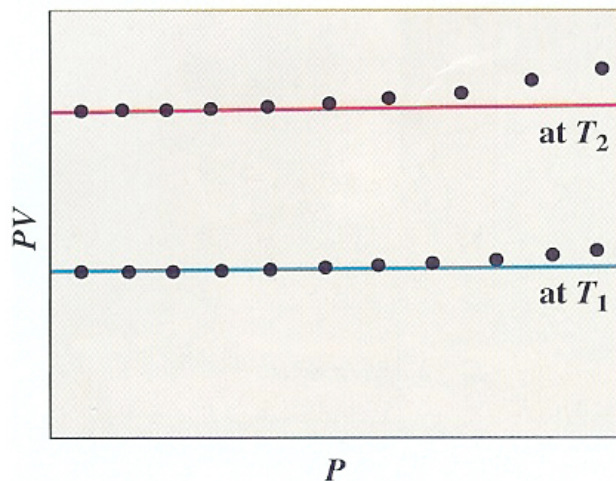


DETERMINING PV BEHAVIOR

Boyle derived part of the Ideal Gas Law by generalizing experimental observations of the PV behavior of gases.

Boyle's Law: The product of the pressure and volume is constant at constant temperature: $PV = C_T$.

A constant that depends on the temperature and the amount of gas.

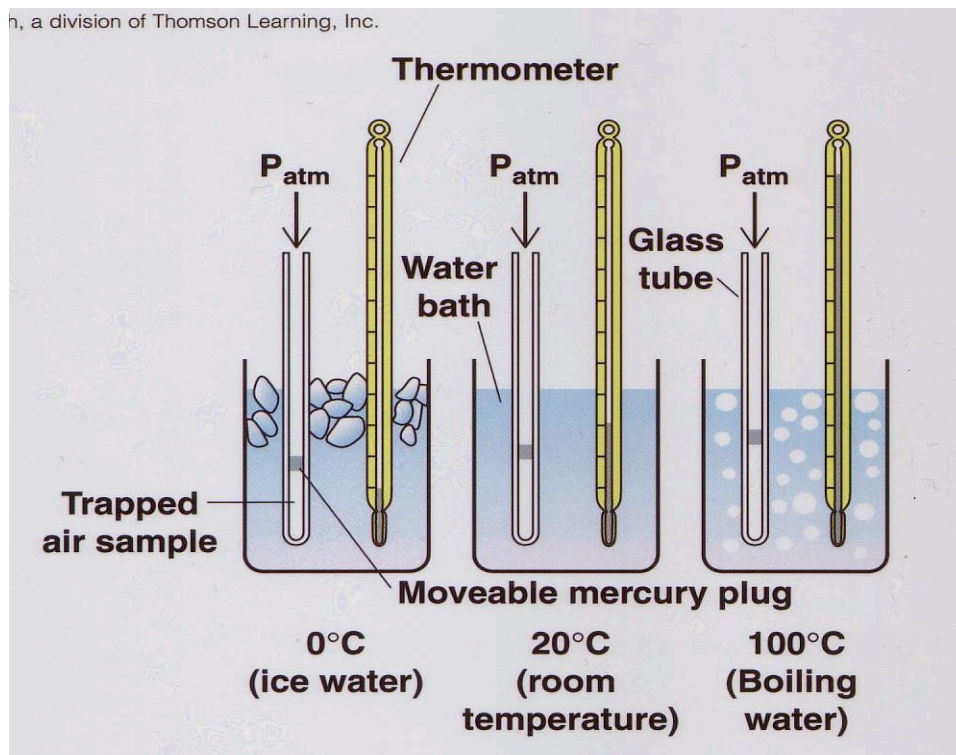


DETERMINING VT BEHAVIOR

Measure gas volume as a function of temperature.



Joseph Gay-Lussac



DETERMINING VT BEHAVIOR

Measure gas volume as a function of temperature.

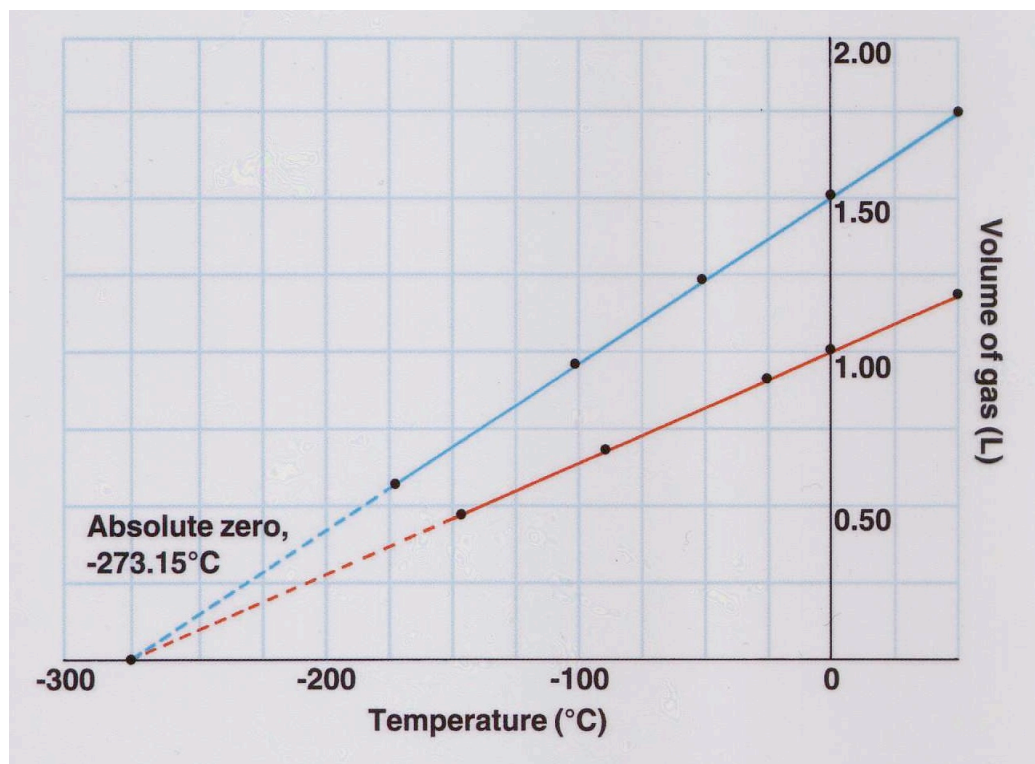
$$V = V_0 + C_p T$$

A constant that depends on the pressure and the amount of gas

$$V = C_p(T - 273.15 \text{ }^\circ\text{C})$$

Leads to the absolute temperature scale:

$$T (\text{K}) = T - 273.15 (^\circ\text{C})$$



DETERMINING VT BEHAVIOR

Charles' Law: The ratio of the volume and temperature is constant at constant pressure: $V/T = C_p$. Or, $V = C_p \times T$.



Invented the hydrogen balloon, but never stated the law that carries his name.

Jacques Charles



THE CONNECTION OF V AND n

A gas at a particular pressure and temperature has a fixed density:

The volume of a gas is proportional to the amount of gas $V = C_{P,T} \times n$. Or, $n/V = 1/C_{P,T}$.

A constant that depends on the pressure and temperature

The amount of gas

The amount of gas can be measured in different units. We will use the number of moles, and the symbol "n" following Avogadro's Law to make this general.

