General Chemistry – Week 5
Gas laws

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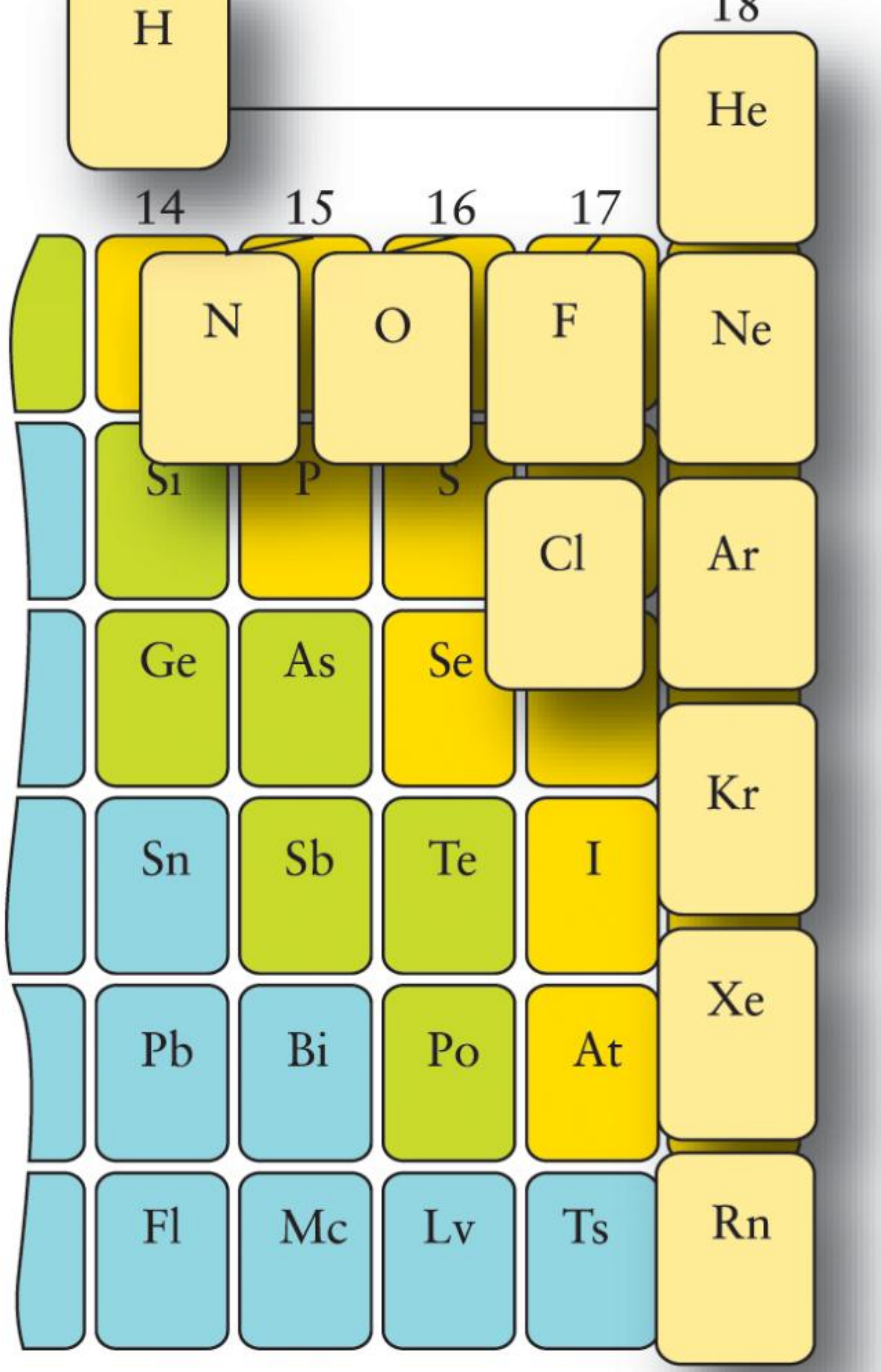


In this Lecture…

You will learn about the gas laws. These will allow us to predict the physical properties of gases.

- These equations describe the nature of a gas.
- Gases are in a ceaseless, random motion and so widely separated that they do not interact with one another.

Overview

- In the previous lectures we investigated the nature of individual atoms, molecules, and ions.

- Now, we begin studying the behavior of bulk matter; gases are a good example of this.

- We apply similar concepts of the behavior of bulk matter when studying:

  Thermodynamics,

  Equilibrium, and

  The Rates of Chemical Reactions.

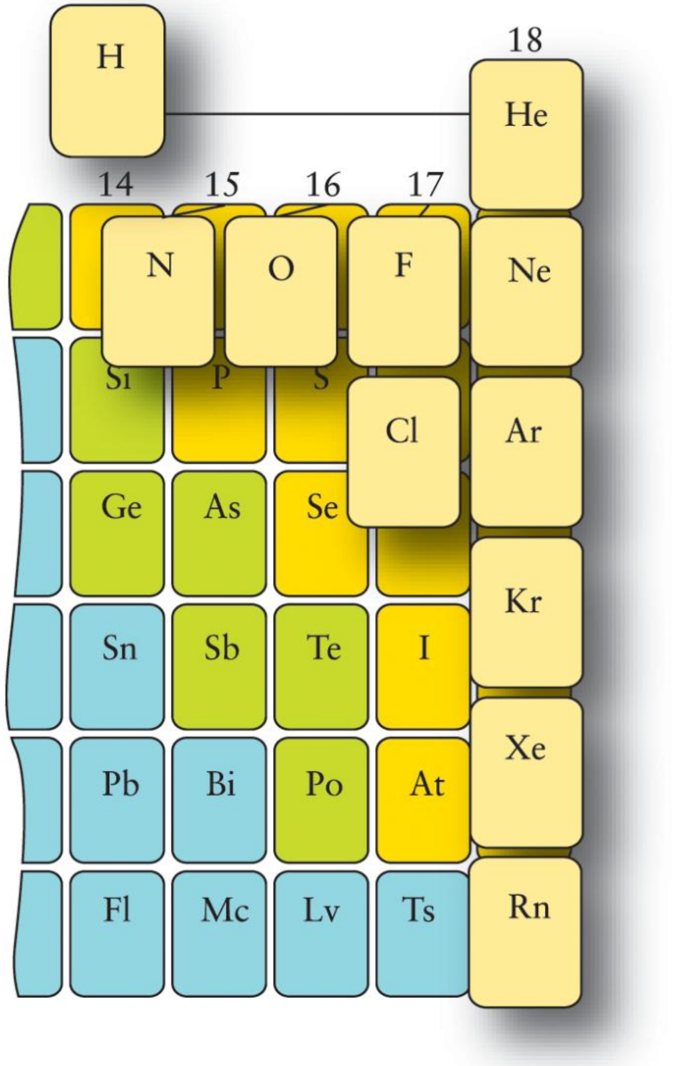
Gases and the Earth

- A thin layer of gas is held by gravity to the Earth’s surface. Half of its mass lies within 5.5 km (3.4 mi) above our heads.
- Viewing Earth as a basketball, the atmosphere is only 1 mm thick. This layer shields us from harmful radiation and supplies us with oxygen, nitrogen, carbon dioxide, and water.

James Thew/Alamy.

The Nature of Gases

- Eleven elements are gases under normal conditions.
- Low molar mass compounds such as carbon dioxide and hydrogen chloride are also gases.
- A remarkable characteristic of gases is that many of their physical properties are very similar, particularly at low pressures, regardless of the identity of the gas.



Observing Gases: Compressibility

- Pushing on a bicycle pump—with your finger over the valve—you can feel the pressure build, as you confine the gases into smaller and smaller volumes.

- The observation that gases are more compressible than solids and liquids suggests that there is a lot of space between the molecules of gases.

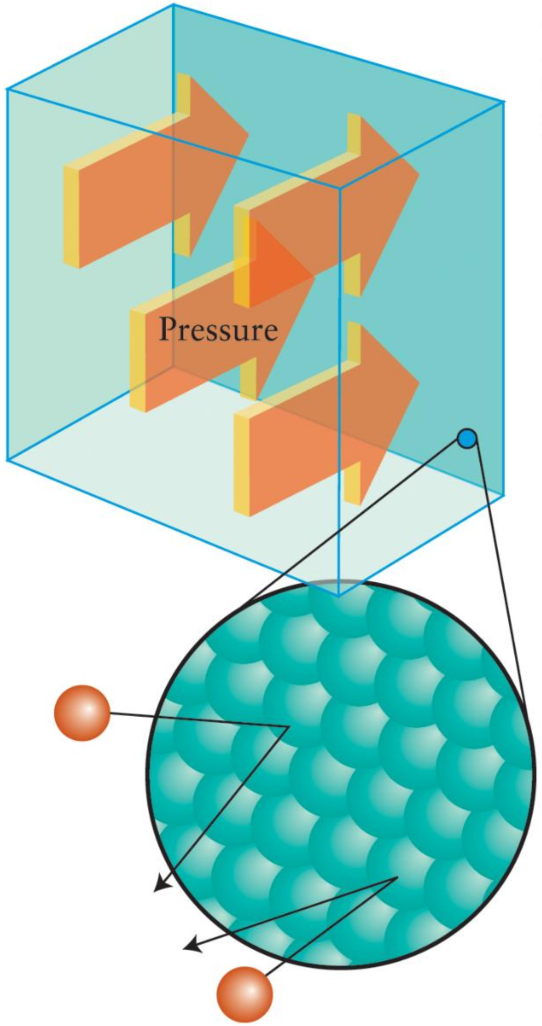
Observing Gases: Motion

- Releasing air from an inflated balloon, we know the gas expands rapidly to fill the space available to it.
- Also, because balloons are spherical we can infer that the motion of the molecules is chaotic, not favoring any single direction.
- Our first primitive picture of a gas could be that gases are a collection of widely spaced molecules in ceaseless rapid chaotic motion.

Pressure: What Causes It?

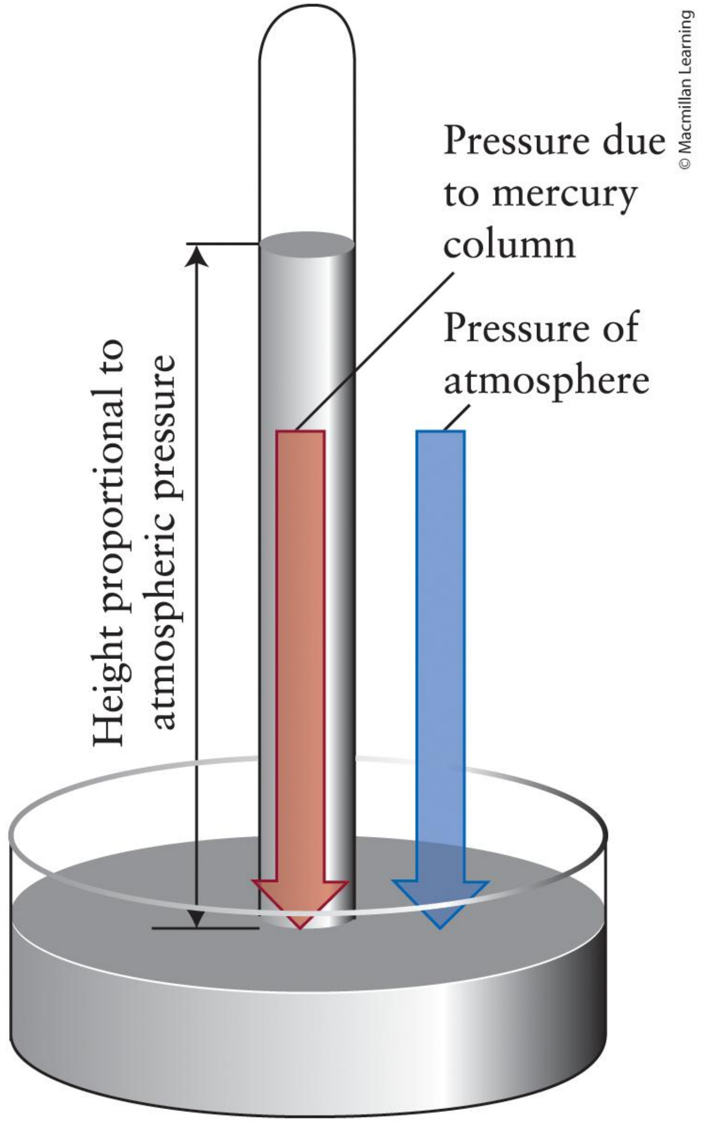
$$\text{pressure} = \frac{\text{force}}{\text{area}} \qquad P = \frac{F}{A}$$

- The SI unit of pressure is pascal, Pa: 1 Pa = 1 kg·m^{-1}·s^{-2}
- Colliding gases exert a pressure on the sides of the container walls
- The more vigorous the motion, the stronger the force and hence the higher the pressure.



The Barometer

- Evangelista Torricelli, seventeenth century, a student of Galileo, made the first barometer (Torricelli means "little tower" in Italian).
- A glass tube, sealed at one end, was filled with liquid mercury. The column was inverted into a pool of mercury. The mercury stopped falling when the weight of the falling mercury was matched by atmospheric pressure weight pushing against the pool of mercury.



Using a Barometer

To find the atmospheric pressure you need to known the height of a tower of mercury.

$$P = \frac{F}{A} = \frac{mg}{A} = \frac{dhAg}{A} = dhg$$

P = pressure

F = force

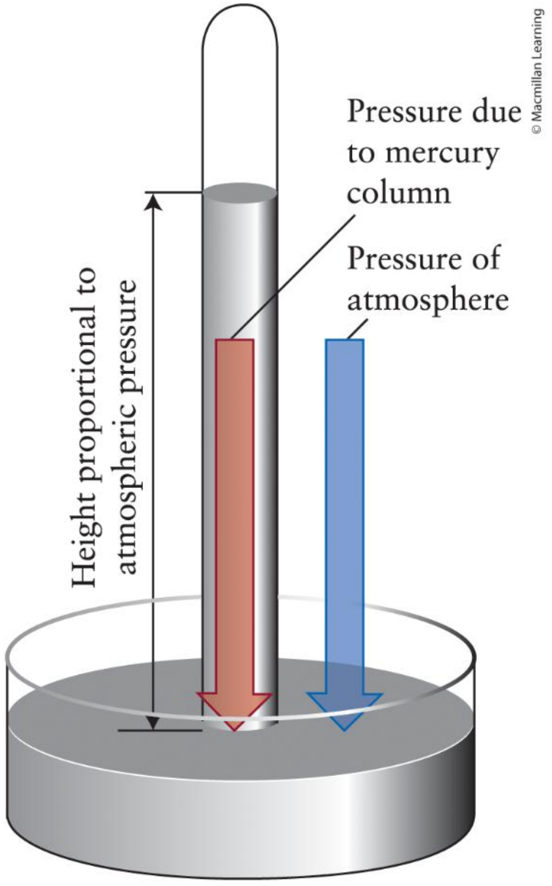
A = area

m = mass

g = gravity (a constant)

d = density

h = height



Alternative Units of Pressure

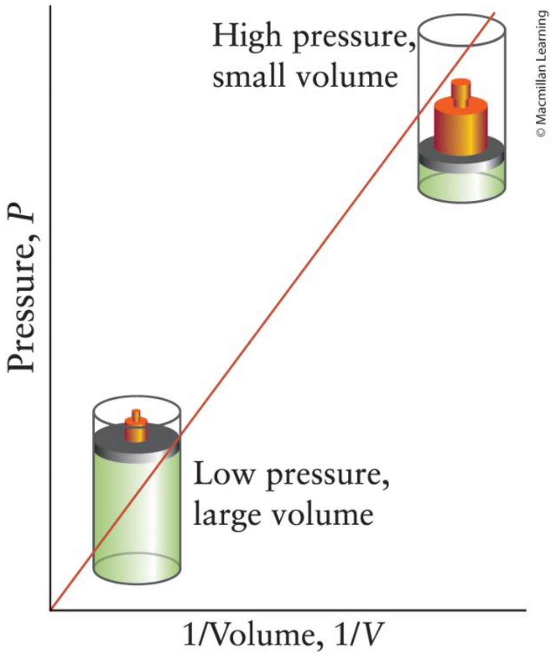
- Although the SI unit of pressure is the pascal (Pa), there are several other units in common use.
- 1 bar = 10^5 Pa
- 760 Torr = 760 mmHg = 1 atm = 14.7 $\text{lbs}\cdot\text{in}^2$ (psi) = 1.01325×10^5 Pa
- The units of mmHg and Torr can be used interchangeably.
- A note on good practice: The name of the unit torr, like all names derived from the names of people, has a lower-case initial letter; likewise, the symbol Torr has an uppercase initial letter.

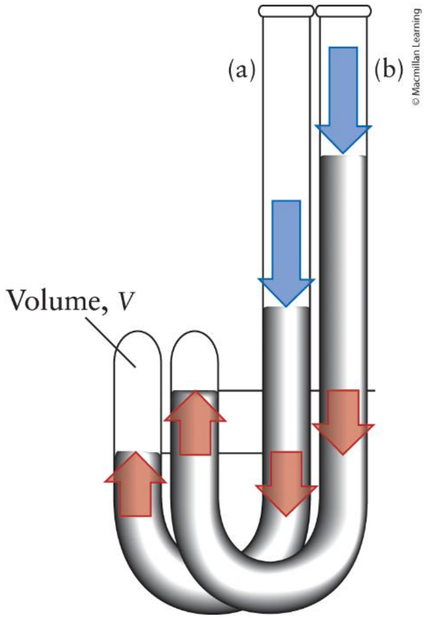
The Gas Laws

- Gas Law properties include pressure, volume, temperature, and moles.
- The first reliable measurements of gases were made by the Anglo-Irish scientist **Robert Boyle** in 1662.
  - He examined the effect of pressure on volume.
- 150 years later, a new pastime, hot-air ballooning, motivated two French scientists, **Jacques Charles and Joseph-Louis Gay-Lussac**, to formulate additional gas laws.
  - Charles and Gay-Lussac measured how the temperature of a gas affects its pressure, volume, and density.
- The Italian scientist **Amedeo Avogadro** made further contributions.
  - He established the relation between the volume and the number of molecules.
  - He was then about to help establish the belief in the reality of atoms.

The Gas Laws: Boyle's Law

- Boyle took a J-shaped tube, with the short end sealed, and poured mercury into the tube.
- The more mercury he added, the more the trapped air was compressed.
- He concluded that at constant temperature, the volume decreases as the pressure increases: ↓V ↑P.
- Boyle's data give a straight line for a plot of P against 1/V.
- Note: An **isothermal** change is one that takes place at constant temp.





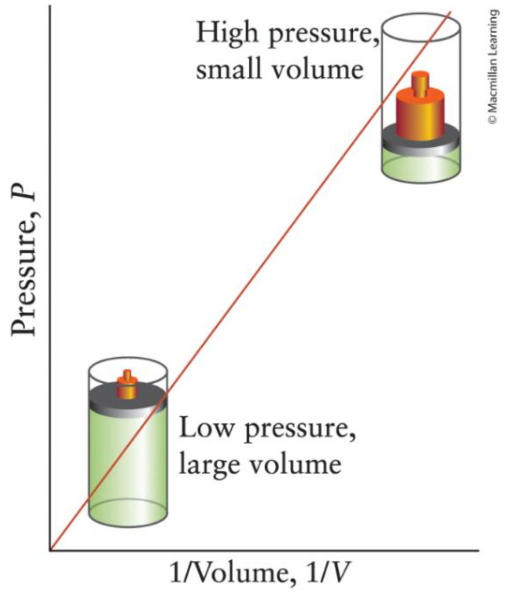
The Gas Laws: Boyle's law

- Scientists look for ways of plotting experimental data to give a straight line; graphs like this are easier to identify, analyze, and interpret.
- Boyle's law implies that volume is inversely proportional to pressure.
- Written as: $\text{Volume} \propto \dfrac{1}{\text{pressure}}$,

  PV = constant

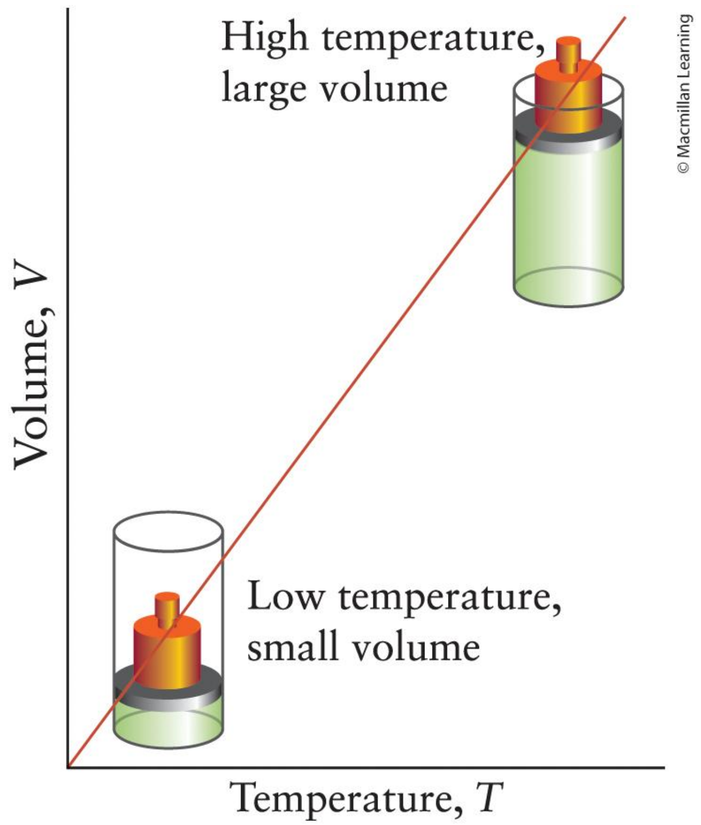
- A common form is $P_2V_2 = P_1V_1$

  The 2's and 1's typically refer to final and initial conditions, respectively.



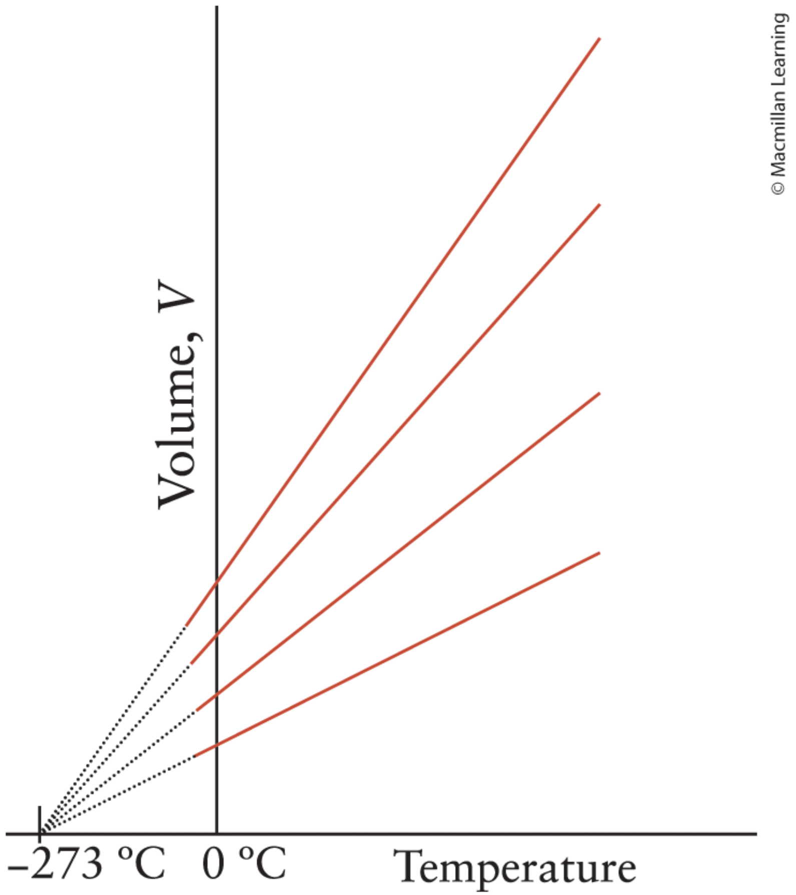
The Gas Laws: Charles's Law

- Charles and Gay-Lussac, hot-air balloon enthusiasts, hoped to improve the performance of their balloons.
- They found that at constant pressure the volume of a gas increases as its temperature is increased: ↑V ↑T .
- A straight-line graph shows a direct relationship when volume plotted against the temperature.
- V/T = constant $\frac{V_2}{T_2} = \frac{V_1}{T_1}$



The Gas Laws: Charles's Law

- Plotting V against T and extrapolating backward, it is found that all gases reach zero volume at −273.15 °C.
- This point cannot be reached in practice, because no real gas has zero volume and all real gases condense to a liquid before reaching such low temperatures.
- Because a volume cannot be negative,
- −273.15 °C must be the lowest possible temperature.
- This corresponds to zero on the Kelvin scale.



Be Sure to Use Temperatures in Kelvin

- Find the volume of 2.0 L of a gas at 50. °C that was heated to 100. °C. Apply Charles's law.

$$\frac{V_2}{T_2} = \frac{V_1}{T_1} \qquad \frac{V_2}{100.\,°\mathrm{C}} = \frac{2.0\ \mathrm{L}}{50.\,°\mathrm{C}} \qquad V_2 = \frac{2.0\ \mathrm{L} \times 100.°\mathrm{C}}{50.°\mathrm{C}} = 4\ \mathrm{L}$$

- Problem: Find the volume of 2.0 L of a gas at 0.0°C that is heated to 100.°C:

$$\frac{2.0\ \mathrm{L} \times 100.°\mathrm{C}}{0.\,°\mathrm{C}} = \text{undefined}$$

- Therefore: $$\frac{2.0\ \mathrm{L} \times 373\ \mathrm{K}}{273\ \mathrm{K}} = 2.7\ \mathrm{L}$$

- The solution is to work all gas laws in kelvin (K = 273.15 + °C)

Avogadro’s Principle

- Avogadro‘s principle: All gases occupy the same volume under the same conditions of temperature and pressure.

$$\textbf{molar volume} = \frac{\text{volume}}{\text{amount}}$$

- Avogadro's principle is

$$V_\text{m} = \frac{\text{volume}}{\text{moles}} = \frac{V}{n}$$

- This is a principle rather than law, because it is based not on observation alone but also on a model of matter—namely that matter consists of molecules. Even though there is no longer any doubt that matter consists of atoms and molecules, it remains a principle rather than a law.

Avogadro's Principle

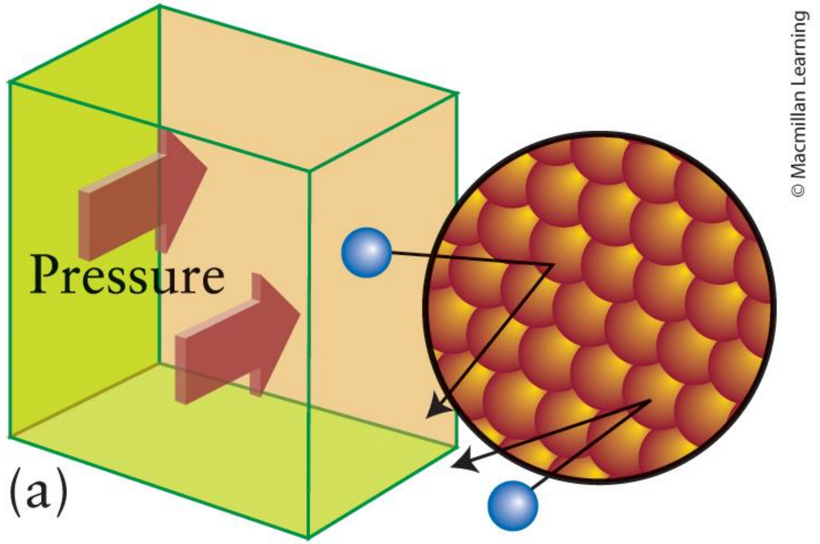
- The molar volume of all gases is close to 22 $L \cdot mol^{-1}$ at 0 °C and 1 atm.

Ideal gas	22.41
Argon	22.09
Carbon dioxide	22.26
Nitrogen	22.40
Oxygen	22.40
Hydrogen	22.43

Summary of Gas Properties

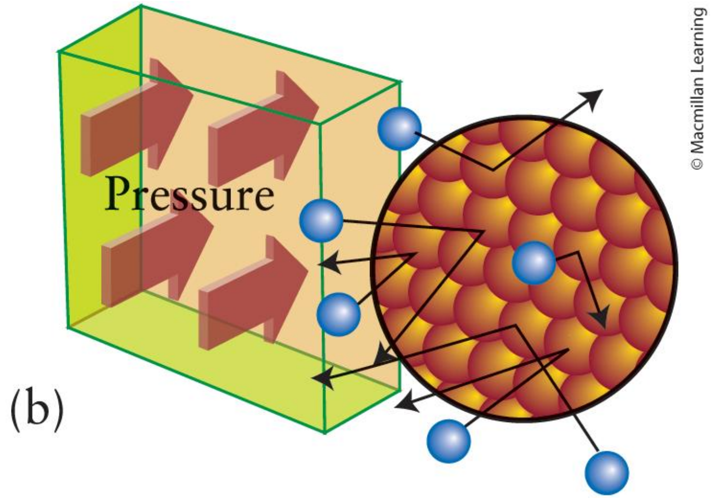
- The effect of temperature on pressure, volume and moles:
- In a container with a fixed volume, as the temperature of a gas increases, the average speed of the molecules increases, which causes the pressure to increase.

- T↑, velocity↑, P↑



Summary of Gas Properties

- At constant pressure, the volume must increase to counteract increases in pressure as the temperature increases, the volume must increase to allow the gases to strike the walls in the same given time interval:
- T↑ velocity↑ V↑
- Avogadro's principle: to keep the pressure constant as more molecules are added to a container, the size of the container must increase:
- n↑ V↑



The Gas Laws: The Ideal Gas Law

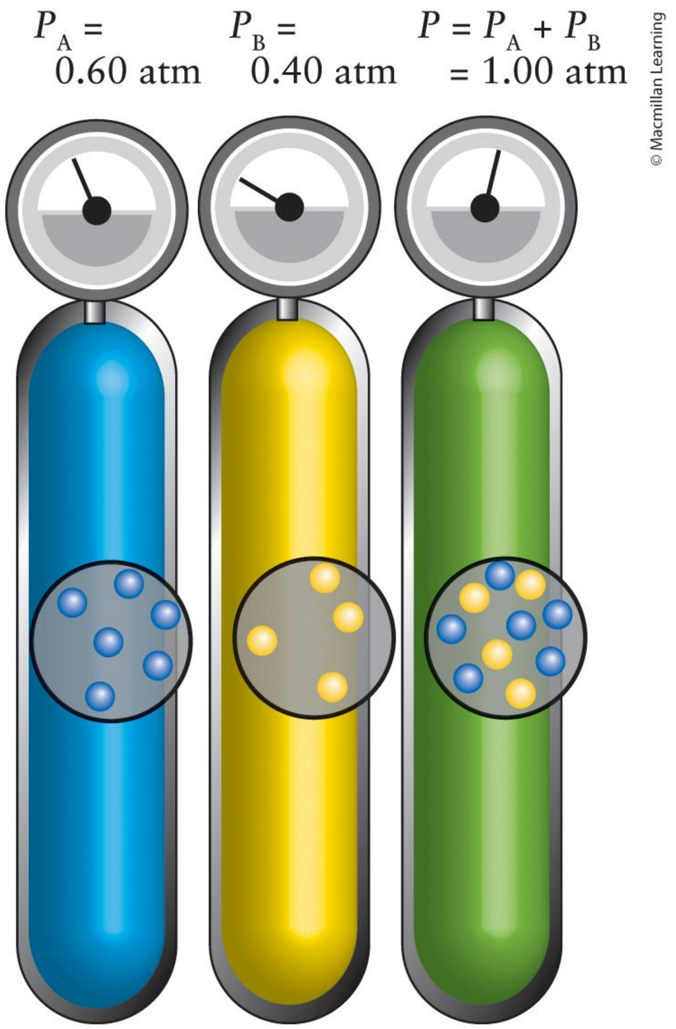
- A gas is a collection of widely-spaced molecules in ceaseless motion.
- The three properties of a gas can all be combined into a single expression relating pressure (P), volume (V), temperature (T), and amount (n) of a gas:
- $PV = \text{constant} \times nT$
- When the constant of proportionality for the laws is written as R, this expression becomes the ideal gas law:
- $PV = nRT$

Limiting Law

- $PV = nRT$
- The constant R is independent of the identity of the gas; we say that it is a “universal constant”. The value of the gas constant can be determined by measuring P, V, n, and T.
- $R = 8.314\ J \cdot K^{-1} \cdot mol^{-1}$
- The ideal gas law is an example of a limiting law, a law that is strictly valid only under certain conditions.
- It is reasonably reliable at normal pressures, and so we can use it to describe the behavior of most gases under normal conditions.

Mixtures of Gases

- The atmosphere of air is a mixture of nitrogen, oxygen, argon, carbon dioxide, and many other gases.
- A mixture of gases behaves like a single pure gas.
- Dalton concluded that the total pressure is the sum of the individual pressures of each gas.



Dalton's Law of Partial Pressures

- Dalton summarized his observations in terms of the partial pressure of each gas.
- The total pressure of a mixture of gases is the sum of the partial pressures of its components:
- $P = P_A + P_B + \ldots$

More on Dalton's Law of Partial Pressures

- The easiest way to express the relation between the total pressure of a mixture and the partial pressures of its components is to introduce the **mole fraction**, x.
- The moles of each gas nA, nB expressed as a mole fraction of gases A and B are:

$$x_A = \frac{n_A}{n_A + n_B + \cdots} \qquad x_B = \frac{n_B}{n_A + n_B + \cdots}$$

- Note that: $x_A + x_B + \ldots + x_N = 1$

More on Dalton's Law of Partial Pressures

- In terms of total pressure and moles of all gases:

$$P_\mathrm{T} = \frac{n_\mathrm{T} RT}{V} = (n_\mathrm{A} + n_\mathrm{B} + \ldots)\frac{RT}{V}$$

- Combine and rearrange RT/V to:

$$\frac{P_\mathrm{T}}{(n_\mathrm{A} + n_\mathrm{B} + \ldots)} = \frac{P_\mathrm{A}}{n_\mathrm{A}}$$

- Rearrange to get

$$P_\mathrm{A} = \frac{n_\mathrm{A} P_\mathrm{T}}{(n_\mathrm{A} + n_\mathrm{B} + \ldots)}$$

- Then assign

$$x_\mathrm{A} = \frac{n_\mathrm{A}}{n_\mathrm{A} + n_\mathrm{B} + \cdots}$$

- We arrive at $P_A = x_A P$. (the same applies to each gas)

Applications of the Ideal Gas Law: Combined Gas Law

- Note that, if the initial conditions of a gas are: $P_1V_1 = n_1RT_1$

- Then a change in conditions is: $P_2V_2 = n_2RT_2$

- Because R is a constant, we can equate the two equations:

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

- This expression is called the combined gas law. However, it is a direct consequence of the ideal gas law and is not a new law.

Standard Temperatures and Pressures

- Standard ambient temperature and pressure (SATP) means exactly 25 °C (298.15 K) and exactly 1 bar. The molar volume of an ideal gas is 24.79 $L \cdot mol^{-1}$, which is about the volume of a cube, 1 ft on a side.
- Standard temperature and pressure (STP) means 0 °C (273.15 K) and 1 atm (both exactly). At STP, the molar volume of an ideal gas is 22.41 $L \cdot mol^{-1}$.
- Note the slightly smaller value: the temperature is lower and the pressure is slightly higher, and so the same amount of gas molecules occupies a smaller volume than at SATP.

Gas Density

- The molar concentration, molarity (c), is the amount of solute (n in moles) divided by the volume (V) of solution.

$$\text{molarity}, c = \frac{\text{mol of solute}}{\text{liters of solution}} = \frac{n}{V}$$

- It follows from the ideal gas law that $(n = \frac{PV}{RT})$:

$$c = \frac{n}{V} = \frac{PV}{RTV} = \frac{P}{RT}$$

Gas Density

- The density, d, of a gas, like that of any substance, is the mass divided by its volume, d = m/V. Because the densities of gases are so low, they are usually expressed in grams per liter ($g{\cdot}L^{-1}$).

- Since mass is moles times the molar mass, m = nM, and
- n = PV/RT, it follows that;

$$d = \frac{m}{V} = \frac{nM}{V} = \frac{(PV/RT)M}{V} = \frac{MP}{RT}$$

Gas Density: Changing V and T

- When a gas is compressed (V↓), its density increases (d↑) because the molecules are confined in a smaller volume.

$$d = \frac{m}{V} = \frac{nM}{V} = \frac{(PV/RT)M}{V} = \frac{MP}{RT}$$

- Upon heating (T↑) the pressure increases the volume occupied by the gas and therefore reduces its density (d↓).
- M = molar mass, m = mass, n = moles,

$$M = \frac{m}{n}$$

Stoichiometry of Reacting Gases

- We might need to know
  - The volume of carbon dioxide produced when a fuel burns, or
  - the volume of oxygen needed to react with a given mass of hemoglobin in the red cells of our blood.
- We answer these questions by using the mole-to-mole calculations we learned in Fundamentals L and M, together with the conversion of moles into volume.

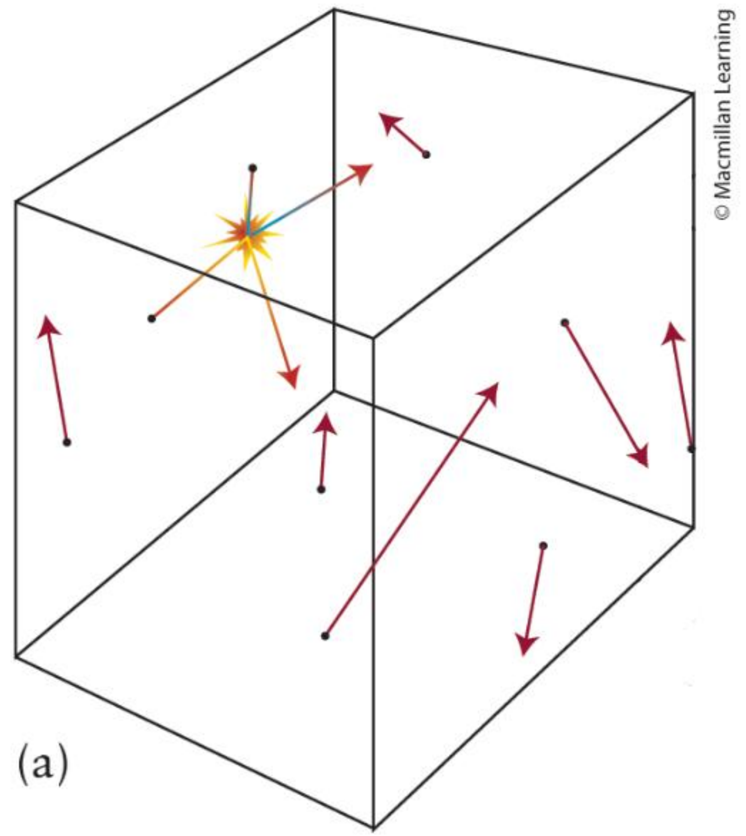
An Example of a Gas Reaction

- Sodium azide, NaN_3, forms large volumes of nitrogen gas; a reaction triggered electrically in air bags.
- $2\ NaN_3(s) \rightarrow 2\ Na(s) + 3\ N_2(g)$
- NaN3 = 65.01 g·mol^{-1}
- 130.02 g $NaN_3 \rightarrow 3$ moles of N_2 gas

Science History Images/Alamy.

The Kinetic Model of Gases

- From our kinetic model (kinetic molecular theory, KMT):
- A gas is in continuous random motion.
- Gas molecules are infinitesimally small.
- They move in straight lines until collision.
- Gas molecules do not influence one another except during collisions.
- The collisions are elastic.



- The kinetic model of a gas allows us to derive the quantitative relation between pressure and the speeds of the molecules.

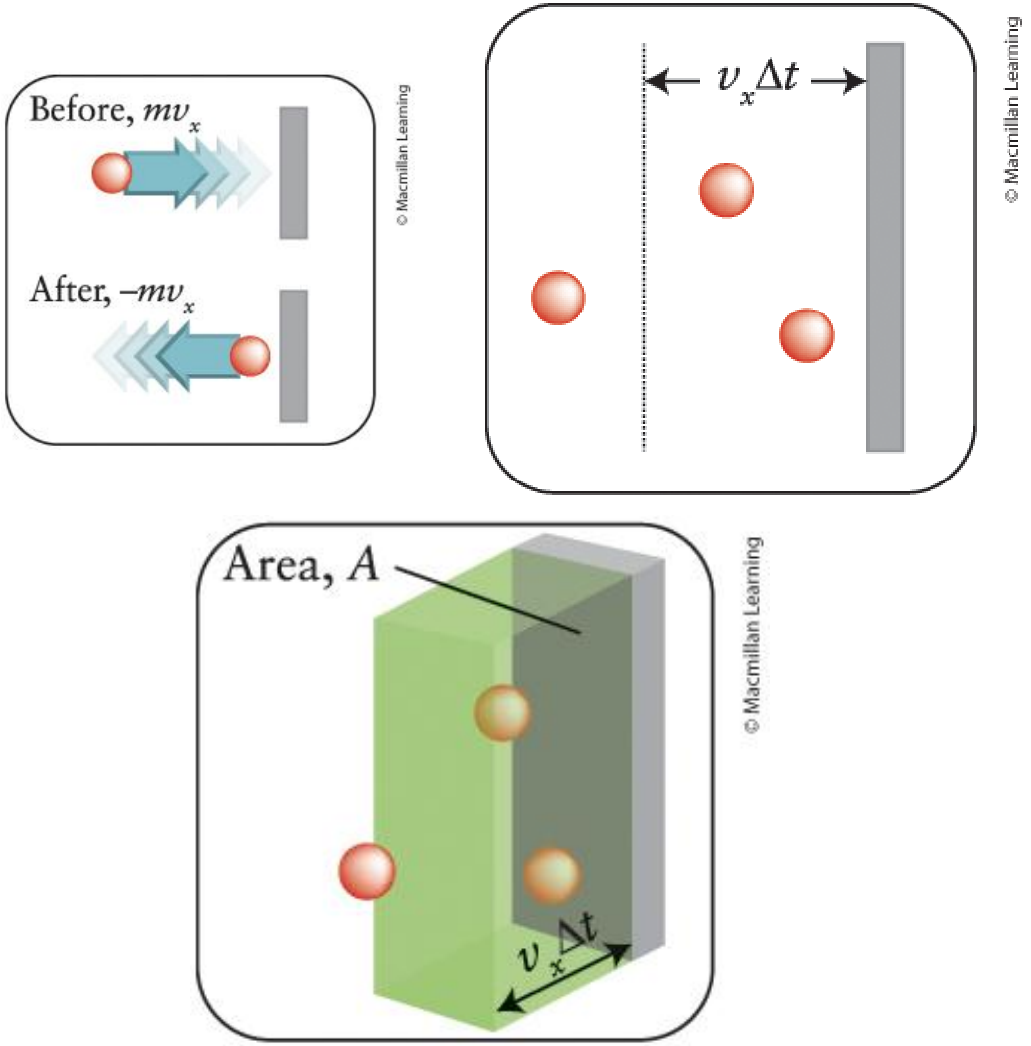
Quantitative Description of the KMT

- If we know how often gases impacts occur and what force they exert, we can calculate the pressure that results.

- Newton’s second law of motion: force is equal to the rate of change of momentum of a particle, or mass times velocity.
- Mass of a molecule: m
- Velocity: v
- Momentum = m × v
- velocity of molecule traveling in x direction: vx
- linear momentum before it strikes the wall: mvx
- momentum after it strikes the wall and changes direction: −mvx

Quantitative Description of the KMT

- The change in momentum of one molecule hitting the wall is $2mv_x$ (v is velocity).
- Any molecules within a distance $v_x\Delta t$ of the wall and traveling toward it will strike the wall during the time interval Δt.
- For a wall with area A, all particles in a volume $Av_x\Delta t$ will reach the wall if they are traveling towards it



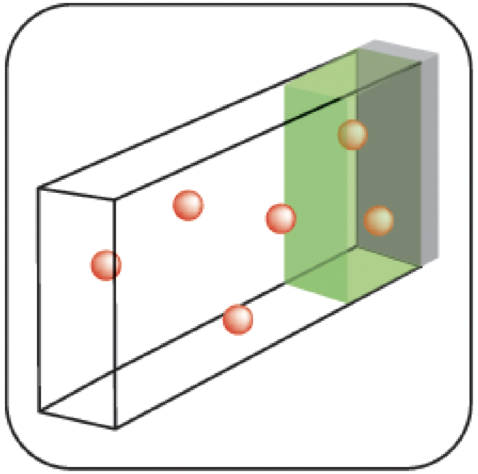
Quantitative Description of the KMT

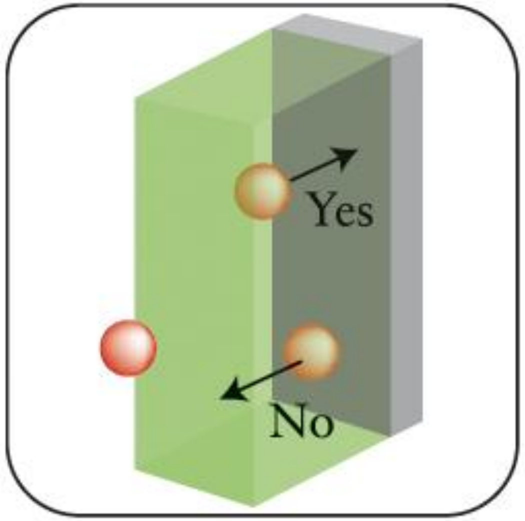
- The number of molecules in a volume ($Av_x\Delta t$) is that fraction of the total volume (V), multiplied by the total number of molecules (N).

$$\frac{NAv_x\Delta t}{V}$$

- Since half the molecules in the box are moving toward the wall on the right and the other half are moving away from that wall, that means the average number of collisions with the wall is half the number in the volume:

$$= \frac{NAv_x\Delta t}{2V}$$



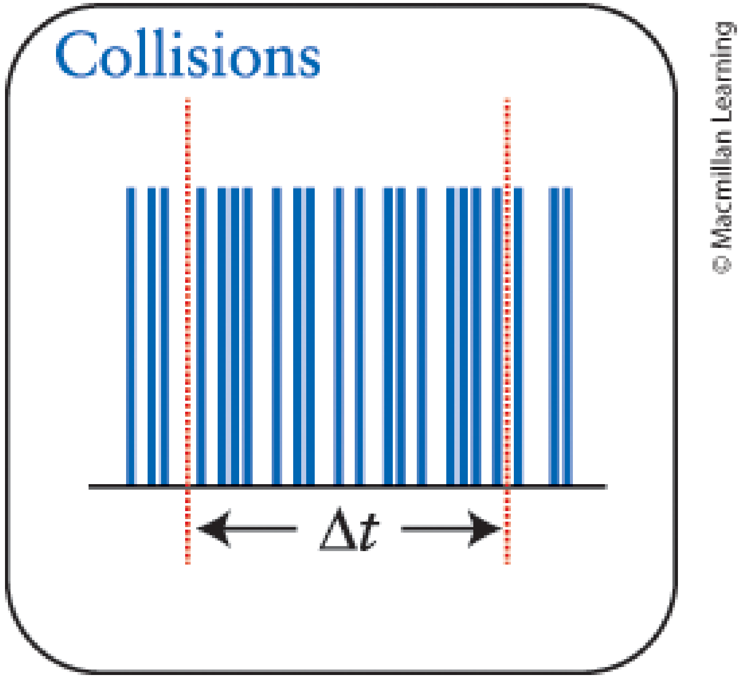


Quantitative Description of the KMT

- The total momentum change in that interval is the change $2mv_x$ that an individual molecule undergoes multiplied by the total number of collisions:

$$= \frac{NAv_x\Delta t}{2V} \times 2mv_x = \frac{NmAv_x^{\,2}\Delta t}{V}$$

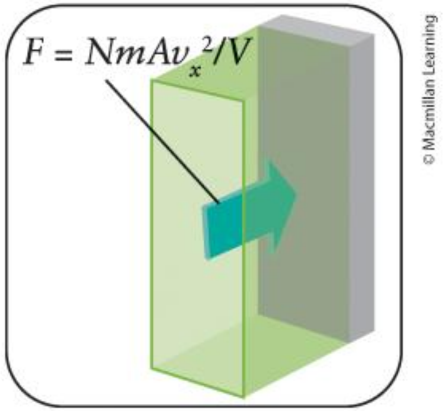
- At this point, we calculate the rate of change of momentum by dividing this total momentum change by the time interval during which it occurs (Δt) and use Newton's second law, that the force is equal to the rate of change of momentum:

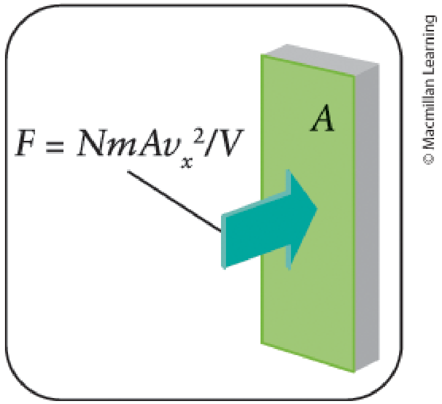


$$\text{Rate} = \frac{NmAv_x^{\,2}\Delta t}{V\Delta t} = \frac{NmAv_x^{\,2}}{V}$$

Quantitative Description of the KMT

- From Newton's second law,
- Force = rate of change of momentum = $NmAv_x^2/V$
- To obtain the observed pressure, P, we need to use the average value of v_x^2 in place of v_x^2 for each individual molecule.
  Therefore, we write



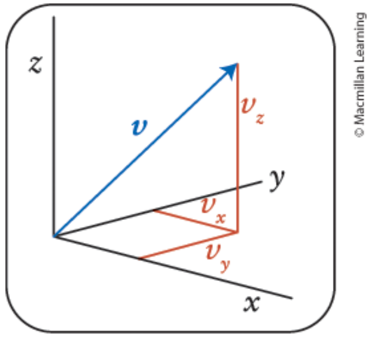


$$\text{Pressure} = \text{force/area} = \frac{NmAv_x^2}{VA} = \frac{Nmv_x^2}{V}$$

$$P = \frac{Nm\langle v_x^2 \rangle}{V}$$

where $\langle v_x^2 \rangle$ is the average value of v_x^2.

Quantitative Description of the KMT



- $\langle v_x^2 \rangle$ can be related to the root mean square speed, $v_{rms} = \langle v_x^2 \rangle^{1/2}$, the square root of the average of the squares of the molecular speeds.
- Therefore, the mean square speed is given by

$$v^2{}_{\mathrm{rms}} = \langle v^2 \rangle = \left\langle v_x{}^2 + v_y{}^2 + v_z{}^2 \right\rangle = \langle v_{\mathrm{x}}{}^2 \rangle + \left\langle v_{\mathrm{y}}{}^2 \right\rangle + \langle v_{\mathrm{z}}{}^2 \rangle$$

- From the Pythagorean theorem, $v^2 = v_x^2 + v_y^2 + v_z^2$

Quantitative Description of the KMT

- However, because the particles are moving randomly, the average of v_x^2 is the same as the average of v_y^2, and the average of v_z^2.
- Because $\langle v_x^2\rangle$, $\langle v_y^2\rangle$, and $\langle v_z^2\rangle$ are all equal, we know that $\langle v^2\rangle=3\langle v_x^2\rangle$; therefore, $\langle v_x^2\rangle = (1/3)v_{rm}s^2$.
- It follows that $$P = \frac{Nmv_{rms}{}^2}{3V}$$

Quantitative Description of the KMT

- The total number of molecules, N, is the product of the amount, n, and Avogadro's constant, NA ; so the last equation becomes,

$$P = \frac{nN_{\mathrm{A}}mv_{\mathrm{rms}}{}^{2}}{3V} = \frac{nMv_{\mathrm{rms}}{}^{2}}{3V}$$

- where m is the mass of one molecule and M = mN_A is the molar mass of the molecules.
- We have deduced that the pressure of a gas and the volume are related by,

$$PV = \frac{1}{3}nMv_{\mathrm{rms}}{}^{2}$$

Quantitative Description of the KMT

- If there are N molecules in the sample and the speeds of these molecules at some instant v_1 , v_2 …. v_N, then the root mean square speed is

$$v_{\mathrm{rms}} = \left(\frac{{v_1}^2, {v_2}^2 \ldots . {v_N}^2}{N}\right)^{\frac{1}{2}}$$

- Since PV = nRT, we set PV = (1/3)nMv_{rms}^2 = nRT. Then, rearrange the equation to get

$$v_{\mathrm{rms}} = \left(\frac{3RT}{M}\right)^{\frac{1}{2}}$$

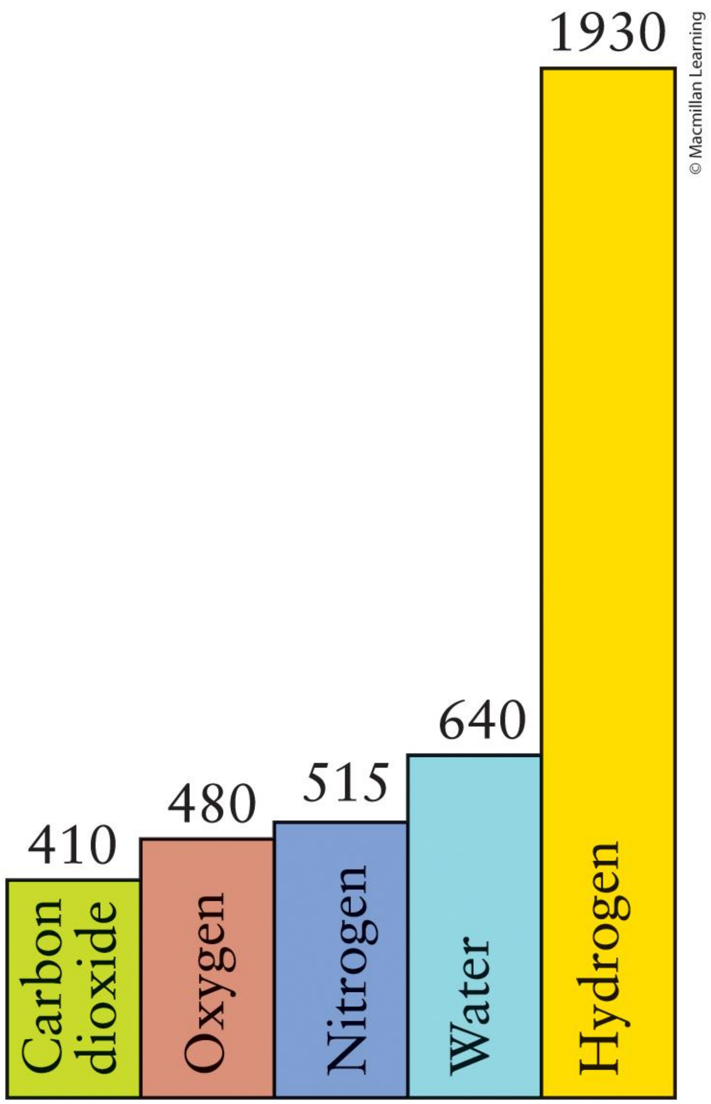
Quantitative Description of the KMT

- And from $v_{rms}^2 = 3RT/M$, it follows that

$$v_{\mathrm{rms}} = \left(\frac{3RT}{M}\right)^{\frac{1}{2}}$$

- The temperature is proportional to the mean square speed of the molecules.

$$T = \frac{M{v_{\mathrm{rms}}}^2}{3R}$$



The Maxwell Distribution of Speeds (1 of 2)

- The root mean square speed equation is like cars in traffic: individual molecules have speeds that vary over a wide range.
- The formula for calculating the fraction of gas molecules having a given speed, v, at any instant was derived by the Scottish scientist James Clerk Maxwell.

$$\Delta N = Nf(v)\Delta v \quad \text{with} \quad f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}} v^2 e^{-Mv^2/2RT}$$

- ΔN is the number of molecules with speeds in the between v and $v + \Delta v$, M is molar mass, and R is the gas constant.

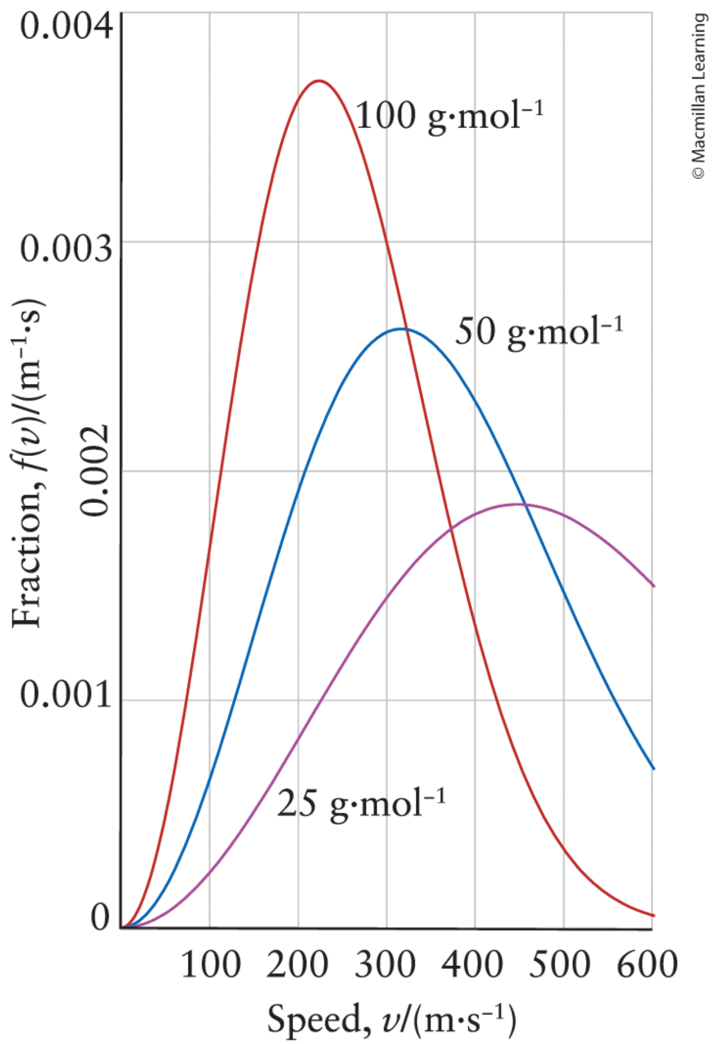
The Maxwell Distribution of Speeds

$\Delta N = Nf(v)\,\Delta v$ with $$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}} v^2 e^{-Mv^2/2RT}$$

- The exponential factor (which falls rapidly toward zero as v increases) means that very few molecules have very high speeds.
- The factor v^2 that multiplies the exponential factor goes to zero as v goes to zero, so it means that very few molecules have very low speeds.
- The factor $4\pi(M/2\pi RT)^{3/2}$ simply ensures that the total probability of a molecule having a speed between zero and infinity is 1.

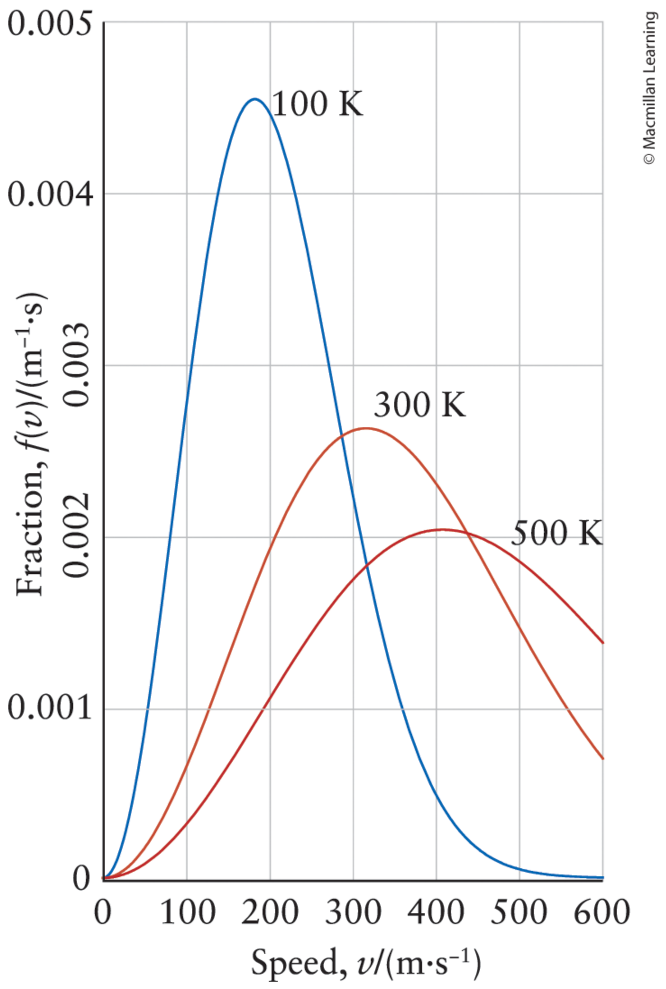
Velocity of Different Masses

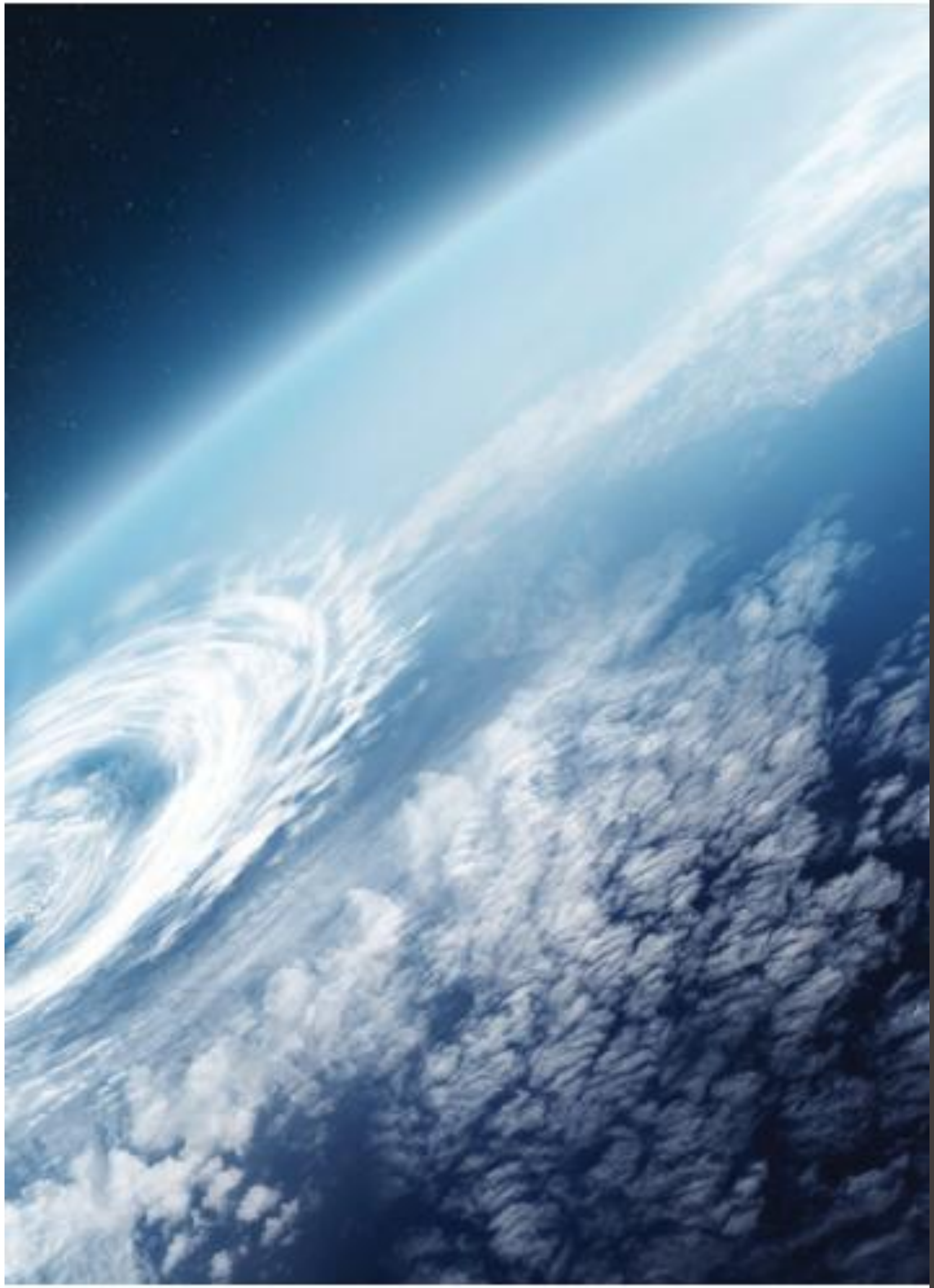
- Maxwell distribution gives the range of molecular speeds for three gases.
- All are for the same temperature, 300 K.
- The greater the molar mass, the lower the average speed.



Velocity of Same Mass

- In the Maxwell distribution, the curves correspond to the speeds of a single substance (of molar mass 50 g·mol−1) at different temperatures.
- The higher the temperature, the higher the average speed and the broader the spread of speeds.





Summary

A student of gases named Drew,
Found Boyle and Charles both quite true.
He said with a grin,
“As pressure drops in—
My volume just *has* to renew!”

ChatGTP’s limerick on gas laws.