

Gas Laws

Chapter 5

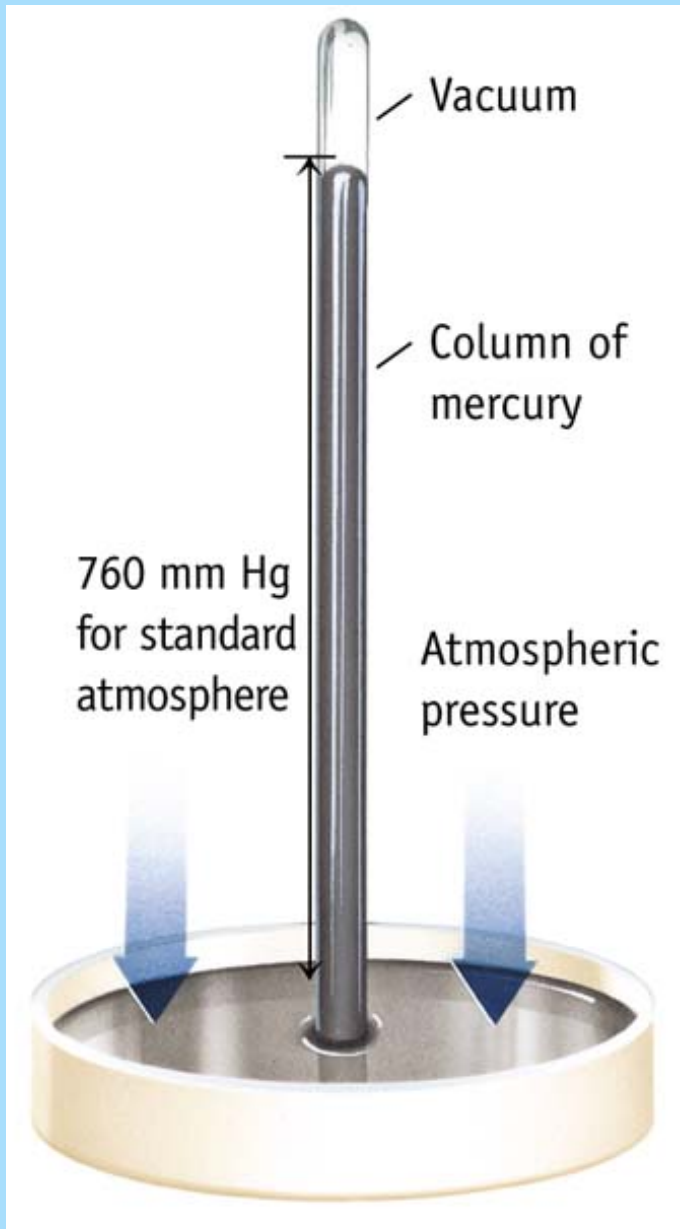
Pressure

- Pressure is defined as the force applied over an area:

$$\text{Pressure (P)} = \frac{\text{Force}}{\text{Area}} = \frac{N}{m^2} = \text{Pascal (Pa)}$$

- Pressure arises from the force of gas particles colliding with surfaces.
- Normal atmospheric pressure is described as one atmosphere.
- $1 \text{ atmosphere (atm)} = 101,300 \text{ Pa} = 101.3 \text{ kPa}$

Barometer

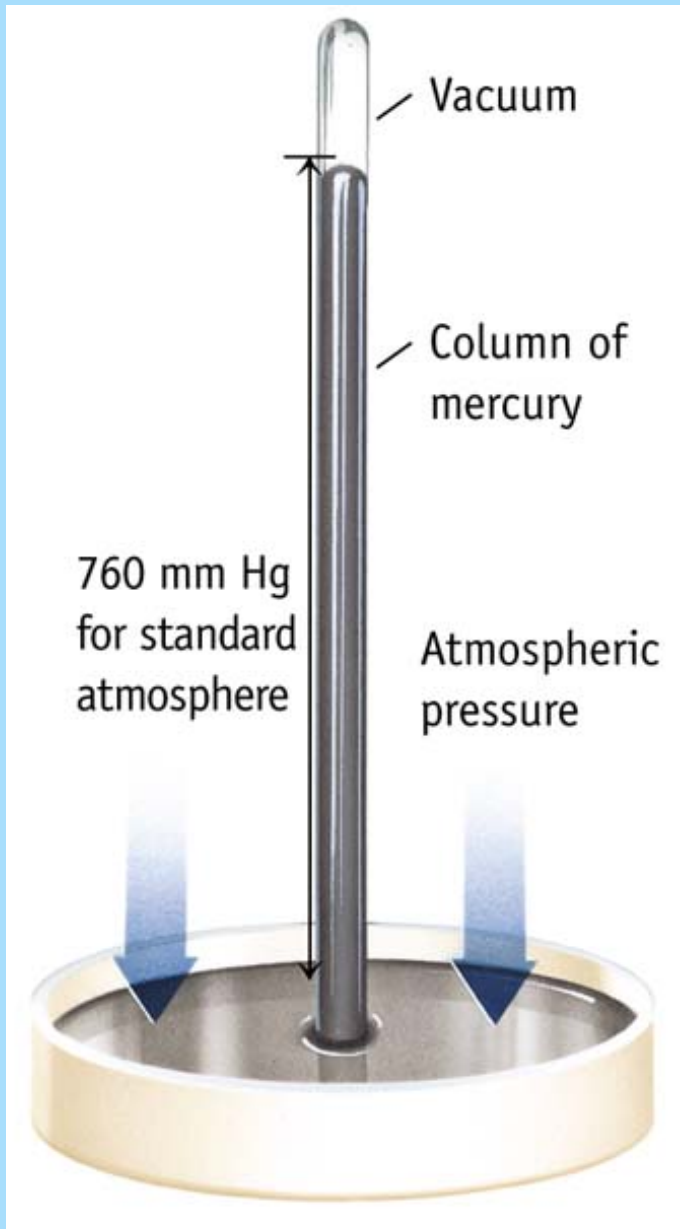


- A barometer measures air pressure based on the height of a column of mercury it can support.

To make a barometer:

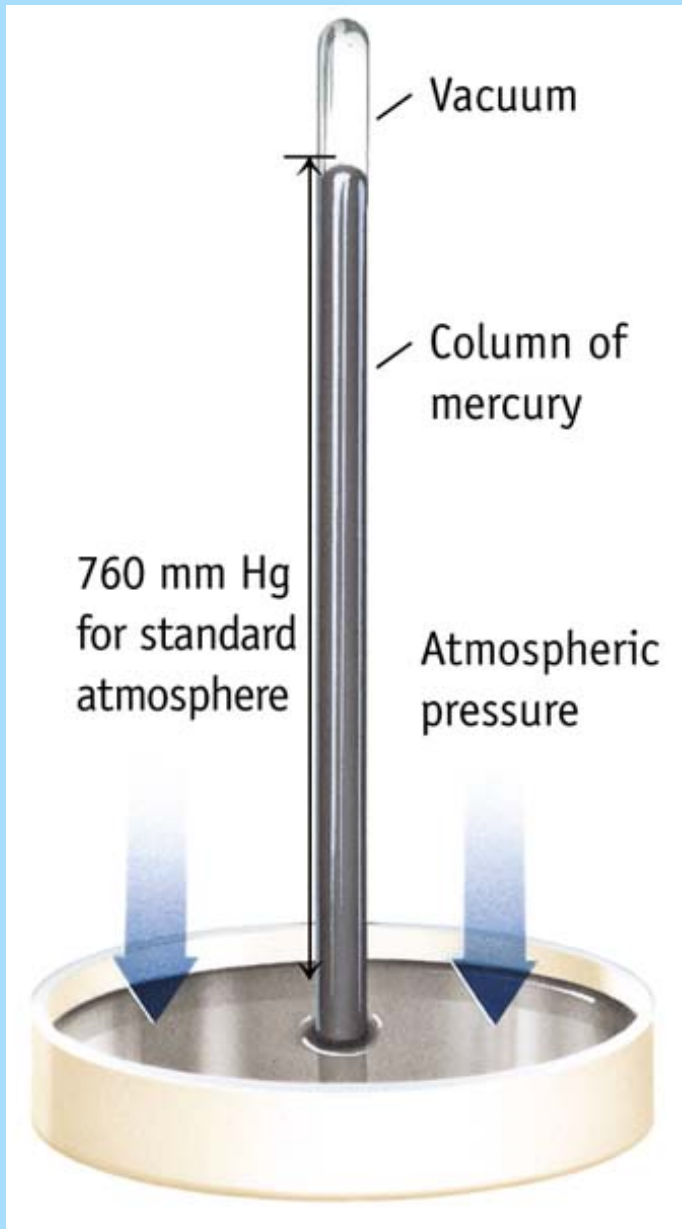
- A glass tube (~ 1 m) is filled with mercury metal and is inverted into a pool of mercury.

Barometer



- The Hg level in the tube will drop – due to gravity – but it will not empty.
- A vacuum (absence of matter) is created as the mercury level drops.
- A column of mercury will remain in the tube. The height of the column (measured in mmHg) is proportional to the pressure of the air pushing down on the pool.

Barometer



- The height of the column will be 760 mm if the pressure of the air is 1 atmosphere.
- $1 \text{ atm} = 760 \text{ mmHg}$
 $= 760 \text{ torrs}$
- The torr is equivalent to the mmHg and is named for the inventor of the barometer, Torricelli.

Pressure (cont.)

- A column of water could be held up much higher than mercury, because it is less dense. One atmosphere pressure could hold a column of water up almost 10 meters.
- Pressure units summary:
 - 1.000 atm = 760.0 mmHg
 - = 760.0 torrs
 - = 101.3 kPa
 - = 101,300 Pa
 - = 14.7 (lbs./in²)
- *Example: Convert 439 mm Hg to kPa.*

Gas Properties

- A gas's properties can be described in a number of ways. Mathematical models of gases use the following properties:
 - Pressure (P)
 - Temperature (T) *in Kelvin*
 - Volume (V)
 - Number of moles (n)
- We will study many relationships of these quantities.

Boyle's Law

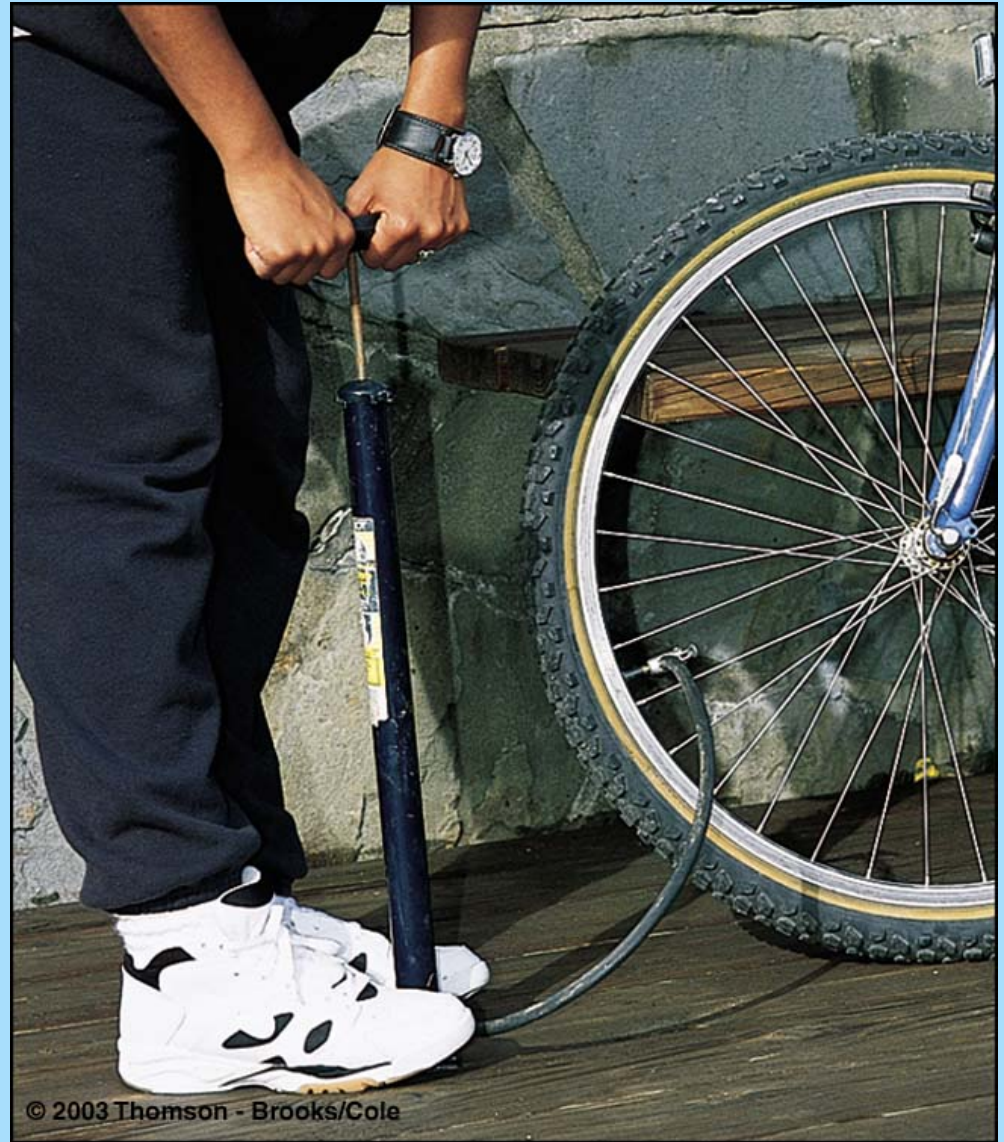
- Robert Boyle studied the relationship between the volume of a gas and its pressure, when the temperature and moles of gas are held constant.
- He found that as the volume of a gas sample is decreased (the gas is compressed), the pressure of the gas will increase by the same factor.
- In other words, pressure and volume are *inversely proportional* – as one increases, the other decreases by the same factor. **$P \propto 1/V$**
- $P V = \text{constant (k)}$

$$P_1 V_1 = P_2 V_2$$

when T and n are constant.

Boyle's Law – a bicycle pump

- As the cylinder of air in the pump is compressed, the pressure of the air inside increases.
- The higher pressure forces air into the tire, and allows us to have a pressure inside the tire greater than the pressure outside.



Charles's Law

- Jacques Charles, a scientist and a balloonist, studied the relationship between the temperature of a gas and its volume, when the pressure and moles of a gas are held constant.
- He discovered that volume and temperature (in Kelvin) are *directly proportional* – as one increases, the other increases by the same factor. $V \propto T$

$$\frac{V}{T} = \text{constant}(k)$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

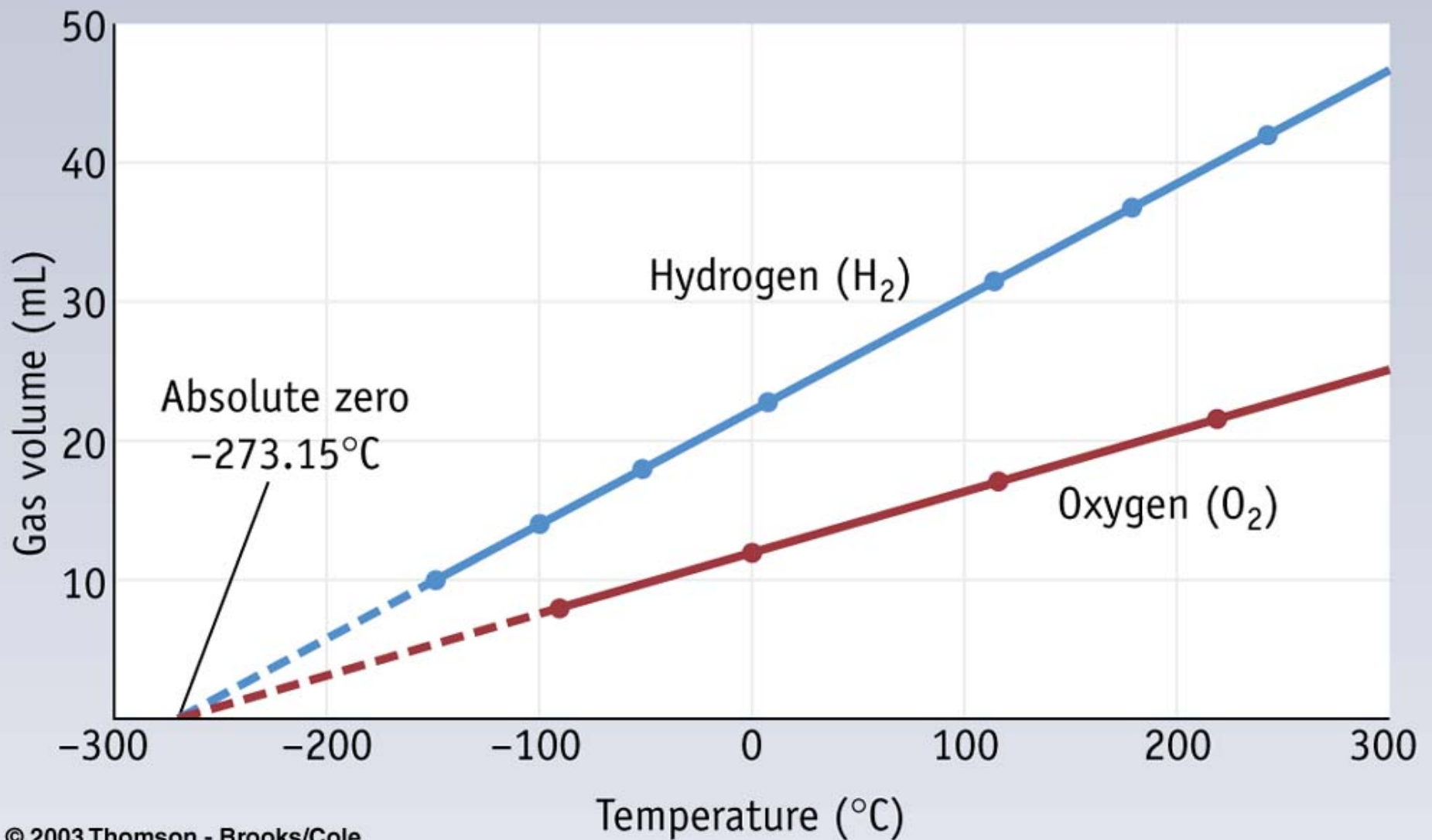
when P and n are constant

Charles's Law and Low Temperature

- When balloons filled with air are put into liquid nitrogen, the gas volume inside is greatly reduced.



Charles's Law and Absolute Zero



Gay-Lussac's Law

- Joseph Louis Gay-Lussac was also a balloonist and studied gases, including the relationship of pressure and temperature under constant volume and mole conditions.
- He determined that pressure and temperature are *directly proportional*. **$P \propto T$**

$$\frac{P}{T} = \text{constant}(k)$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

when V and n are constant

Combined Gas Law

- Often, pressure, volume, and temperature are all variables.
- We can simply combine the three gas laws just described into one relationship when moles are constant.
- Any of the three laws can be derived from this one by canceling the property that is held constant.

$$\frac{PV}{T} = \text{constant}(k)$$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

when n is constant

Example Problems

- If the pressure of a confined gas is tripled while its temperature remains constant, what change will be observed?
- At constant temperature, 10.0 L of N_2 at 0.983 atm is compressed to 2.88 L. What is the final pressure of N_2 ?
- A sample of gas occupies 175 mL at 22 °C and 218 mm Hg. What is the pressure of the gas if the volume is decreased to 122 mL and the temperature increased to 75 °C?

Avogadro's Law

- Amedeo Avogadro made many contributions to chemistry, among them his study of gases.
- He determined that the number of moles of a gas is *directly proportional* to the volume of the sample, when pressure and temperature remain constant. $n \propto V$
- Avogadro found this held true for any gas and that the volume depended only on the number of moles and not the mass of the gases involved.

$$\frac{V}{n} = \text{constant}(k)$$

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

when P and T are constant

- We have already discussed an application of this law: **At STP, 1.00 mole of any ideal gas occupies 22.4 Liters.**

Ideal Gas Law

- The above laws are good for describing the behavior of a gas under changing conditions.
- However, with all four properties of gases related, we can put them together into an equation to describe any sample of an ideal gas.

$$\frac{PV}{nT} = \text{constant (R)}$$

R is the universal gas constant – it is the same for all samples of ideal gases.

- Rearranging, we get the standard form of the ideal gas law:

$$PV = nRT$$

Gas Law Constant

- R is a constant for all gases. The value of R depends on the units we use for the various properties.
 - Volume = Liter (**L**)
 - Temperature = Kelvin (**K**)
 - Number of moles = moles (**mol**)
 - Pressure units vary. We commonly use:
atm, Pa, kPa, mmHg

$$R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} = 62.37 \frac{\text{L} \cdot \text{mmHg}}{\text{K} \cdot \text{mol}} = 8314 \frac{\text{L} \cdot \text{Pa}}{\text{K} \cdot \text{mol}}$$
$$= 8.314 \frac{\text{L} \cdot \text{kPa}}{\text{K} \cdot \text{mol}} = 8.314 \frac{\text{J}}{\text{K} \cdot \text{mol}}$$

Example Problems

- The pressure in a 10.0 L flask containing only propane is 0.912 atm at 78 °C. How many moles of propane are in the flask?

- A 50.0 L cylinder of He has a pressure of 151 atm at 298 K. What mass of He is inside the cylinder?

Gas Stoichiometry

- The volume of gases are related to the number of moles present.
- For gases at STP, we know that there are 22.4 L / 1 mole of any ideal gas.
 - **Standard Temperature = 0° C = 273.15 K**
 - **Standard Pressure = 1.000 atm**
- However, we will not always study reactions under these conditions. In those cases we can use the ideal gas law to relate moles and volume (or other properties) of gases for use in a stoichiometry problem.

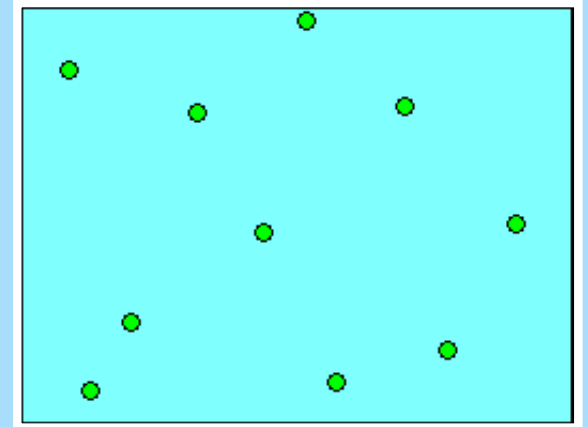
Dalton's Law of Partial Pressures

- For a mixture of gases, the total pressure of the system is the sum of the pressures that each gas exerts individually.

$$P_{\text{TOTAL}} = P_1 + P_2 + P_3 + \dots + P_n$$

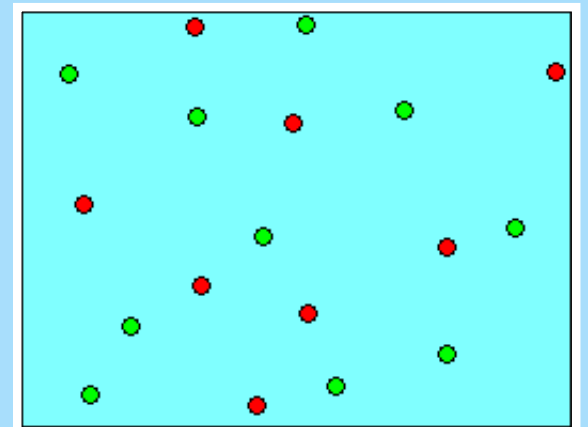
- In the top container, the total pressure of the system is the pressure exerted by the green gas particles.

$$P_{\text{TOTAL}} = P_{\text{green}}$$



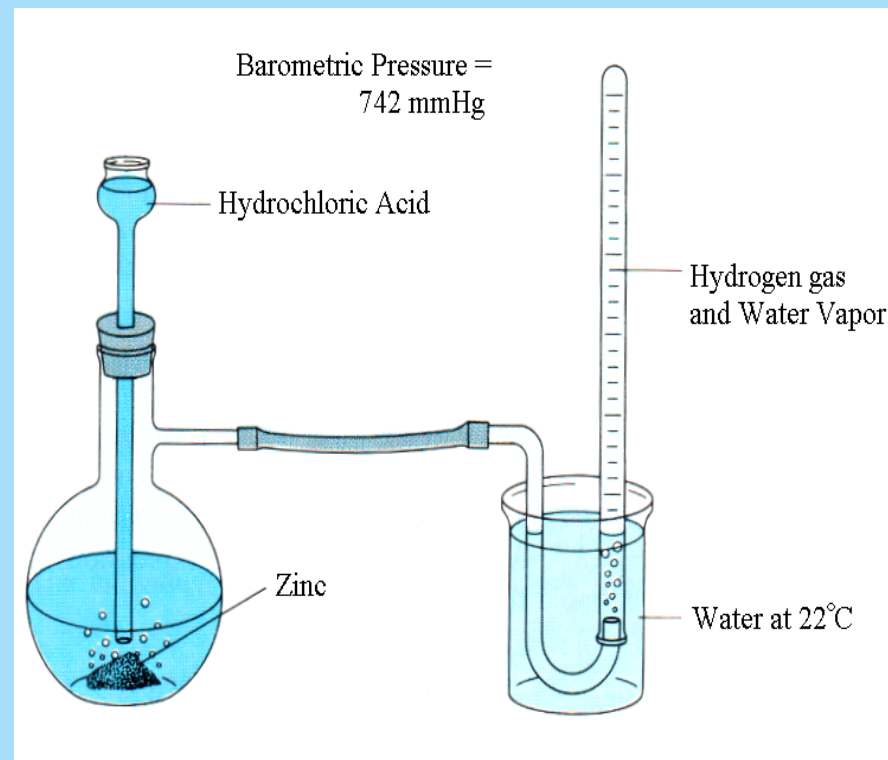
- In the bottom container of the same size, the same number of green gas particles are present, but red gas particles have been added. Both the green and red gas particles exert a pressure on the walls of the container.

$$P_{\text{TOTAL}} = P_{\text{green}} + P_{\text{red}}$$



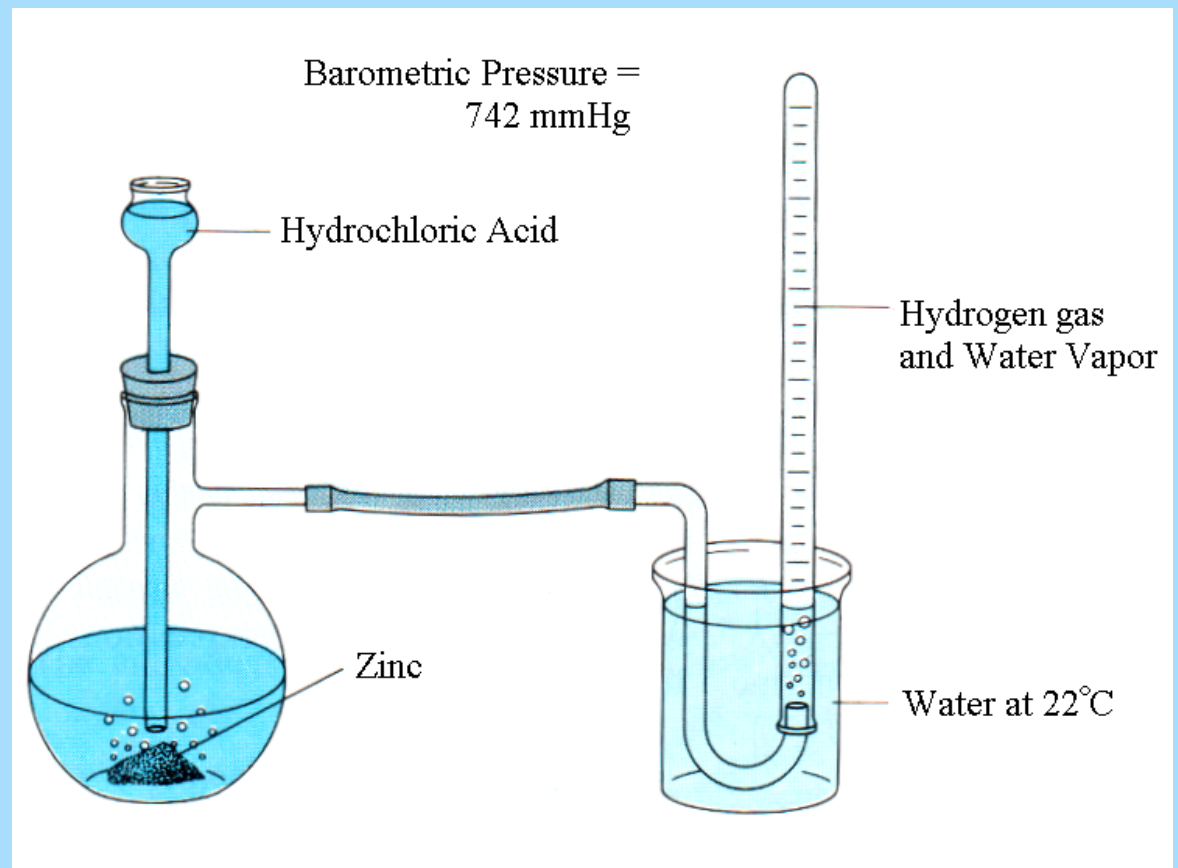
Dalton's Law Application: Gas collection over water

- When a gas is collected over water, water vapor exerts a significant pressure that we must account for.



- In the diagram above, hydrogen (H_2) is produced by the reaction of Zn metal and HCl.
- The hydrogen gas displaces water from the eudiometer tube.

- When the height of the gas collection tube is adjusted to the same level as the water in the beaker, the total pressure of the gas inside is equal to the pressure of the air outside.



- Inside the tube, both $\text{H}_{2(g)}$ and water vapor, $\text{H}_2\text{O}_{(g)}$, are present.

- $P_{\text{atmosphere}} = P_{\text{TOTAL}} = P_{\text{H}_2} + P_{\text{H}_2\text{O}}$
- From the diagram, $P_{\text{atm}} = 742\text{mmHg}$
- At 22°C , $P_{\text{H}_2\text{O}} = 19.8\text{mmHg}$
- $P_{\text{H}_2} = P_{\text{atm}} - P_{\text{H}_2\text{O}}$
 $= 742\text{mmHg} - 19.8\text{mmHg}$
 $= 722\text{mmHg}$

Mole Fraction and Partial Pressures

- The mole fraction (χ) of a gas is the ratio of a given component to the total mixture:
- We can use the concept of mole fraction and the ideal gas law to relate the pressure of a specific gas to the total pressure of the system.

$$\chi_1 = \frac{n_1}{n_{\text{TOTAL}}} = \frac{n_1}{n_1 + n_2 + n_3 + \dots}$$

$$n = \frac{PV}{RT} \quad V, T, R \text{ are constant}$$

$$\chi_1 = \frac{\frac{P_1 V}{RT}}{\frac{P_{\text{TOTAL}} V}{RT}} = \frac{\frac{P_1 V}{RT}}{\frac{P_1 V}{RT} + \frac{P_2 V}{RT} + \frac{P_3 V}{RT} + \dots}$$

$$\chi_1 = \frac{P_1}{P_{\text{TOTAL}}}$$

$$P_1 = \chi_1 P_{\text{TOTAL}}$$

Density of Gases

Kinetic Molecular Theory (of gases)

1. Particle volume is very small relative to the distance between particles
2. Particles are in constant motion. Pressure arises from collisions with a surface.
3. Particles are assumed to have no intermolecular interactions – they do not attract or repel other particles.
4. Average kinetic energy (KE) of particles is directly proportional to the Kelvin temperature.

KMT (continued)

- The KMT applies only to IDEAL gases.
- In reality, all gases are REAL gases.
- Real gases approach ideal behavior at low pressure and high temperature.

Temperature, molar mass, and KE

- From the KMT, we know $T \propto KE_{\text{avg}}$
- Using the ideal gas law ($PV=nRT$) and the kinetic energy equation ($KE = \frac{1}{2} mv^2$), we can derive the relationship:

$$KE_{\text{avg}} = \frac{3}{2} RT$$

Root-mean-square Velocity (u_{rms})

- Molecules (or particles) of a gas in a given sample do not all move with the same speed.
- However, it is convenient to talk about the average speed of particles to relate to temperature and molar mass.
- The average speed can best be represented by the root-mean-square velocity:

$$u_{rms} = \sqrt{u^2}$$

Root-mean-square velocity (cont.)

- Relating the equations for kinetic energy:

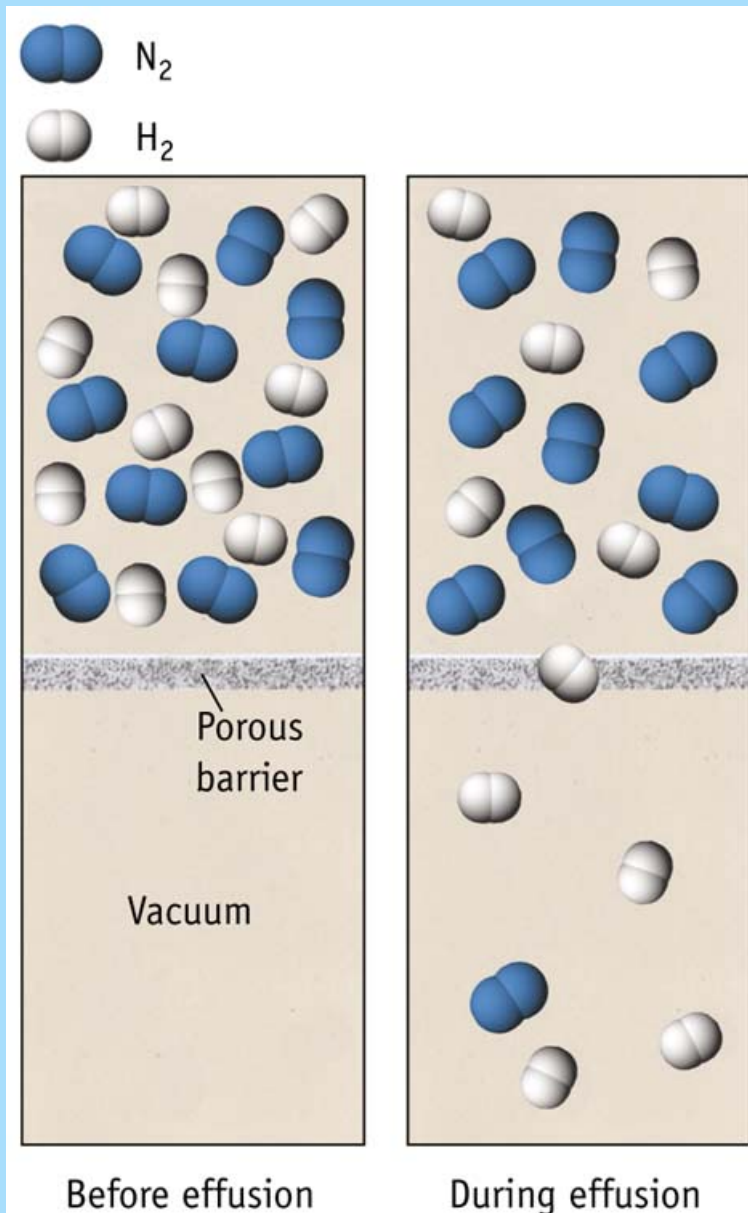
$$KE_{\text{avg}} = \frac{3}{2} RT = N_A \left(\frac{1}{2} m \overline{u^2} \right)$$

- We can derive:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} \quad \text{where } M = \text{molar mass}$$

- From this expression, we can see that the molar mass of the gas and the speed of particle motion are inversely related: the larger the molar mass of a gas, the slower it moves.

Effusion and Diffusion



- Effusion is the passage of molecules through a small hole into a vacuum chamber.
- From the u_{rms} equation, we know that speed of particles moving is inversely related to their molar masses – more massive particles effuse more slowly.
- Effusion (and diffusion) rates are also inversely related to molar masses.

Effusion and Diffusion

- Diffusion is the mixing of gas particles in a sample.
- Diffusion is related to effusion, but is not as easily measured.
- An example of diffusion would be cologne sprayed on one side of the room and, minutes later, it can be smelled across the room.

Effusion rates and Molar Masses

- Because the rate of effusion is directly proportional to the root-mean-square velocity, we can derive the following equation:

$$\frac{\text{rate}_A}{\text{rate}_B} = \sqrt{\frac{M_B}{M_A}}$$

- Notes:
 - Always pay attention to the inverse nature of the equation.
 - Rates of effusion must be in units of moles or particles (not mass) per unit time for the relationship to work.

Examples: Effusion Rates and Molar Masses

- How many times faster will H_2 through an opening than He?
- What is the molar mass of a gas if it effuses through an opening at the rate of 3.83×10^{-4} mol/s when oxygen gas effuses through the same hole at a rate of 7.04×10^{-4} mol/s?

Real Gases

- All gases are real gasses.
- The ideal gas law assumes that atoms and molecules have no volume – they are “point” masses.
- However, at low temperature and high pressure, this approximation is not valid.
- The real gas law accounts for the true volume of particles, with a correction factor, b , in the volume term of the ideal gas law

$$V - nb$$

where V =volume of sample

n = the number of moles a particular gas

and b is specific to each gas

Real Gases

- The ideal gas law assumes that there are no intermolecular interactions (attraction or repulsion) between molecules.
- However, at low temperature and high pressure, this approximation is not valid because particles are moving more slowly and are closer together.
- The real gas law accounts for these interactions with a correction factor, a , in the pressure term.

$$P_{\text{obs}} + a \left(\frac{n}{V}\right)^2$$

where P_{obs} = measured pressure

V = volume of sample

n = the number of moles a particular gas

and a is specific to each gas

Van der Waal's Equation

- Real Gas Law: by substituting the corrected pressure and volume terms into the ideal gas law, we get:

$$\left[P + a \left(\frac{n}{V} \right)^2 \right] \cdot (V - nb) = nRT$$

- Rearranging:

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

- The values of a and b are specific to the gas and are collected in tables.
- The pressure of each gas in a real gas sample must be determined individually and related through Dalton's Law.

Example: Real Gas

Calculate the expected pressure of if 12.00 mol of ammonia gas were compressed into a 10.0-L tank at 23.5°C:

- Using the ideal gas law:
- Using the van der Waal's equation :
for NH_3 ,
 $a = 4.17 \text{ atm}\cdot\text{L}^2/\text{mol}^2$
 $b = 0.0371 \text{ L/mol}$