

Chapter 5: Gases (Ch 10 in Jespersen, Ch 5 in Chang)

Elements that exist as **gases** (at 25 °C and 1atm) are shown in blue.

1A																		8A
H																		He
2A												3A	4A	5A	6A	7A		
Li	Be											B	C	N	O	F	Ne	
Na	Mg																	
		3B	4B	5B	6B	7B	8B			1B	2B							
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg								

Our atmosphere is: Nitrogen 78%, Oxygen 21%, Argon 0.9%, Carbon Dioxide 0.03%, Water vapor 0.0 to 4.0%.

Trace gases include neon, helium, krypton, and xenon.

Characteristics of Gases

- *expand* to fill container.
- can be *expanded* or *compressed*.
- form *homogeneous* mixtures (e.g. air).
- have much *lower densities* than liquids and solids.
- gases only occupy a *small* fraction of the total volume; they behave as if the other molecules were absent.
- they can exert a *pressure* (e.g. balloons).
- the pressure depends on the *amount* of confined gas.
- the pressure will rise and fall with *temperature*.

The fact that gases are readily compressible and immediately fill the space available to them suggests that molecules of gases are **widely separated** and in **ceaseless chaotic motion**.

Even though gases can vary tremendously in their *chemical* properties, **essentially all gases obey the same set of physical properties**.

These four inter-related physical properties are **Pressure, Volume, Temperature** and **Amount**.

Pressure (P)

Pressure is a *force per unit area*.

Force = **mass** (kg) x **acceleration** (ms^{-2}).

The SI unit of **force** is the **Newton, N**.

The SI unit of **Pressure** is the **Pascal, Pa**.

$$P = \frac{F}{A} = \frac{\text{kg} \frac{\text{m}}{\text{s}^2}}{\text{m}^2} = \frac{\text{N}}{\text{m}^2} = \text{Pa}$$

$$\text{Units of } F = N = \text{kg} \frac{\text{m}}{\text{s}^2}$$

Pressures can also be expressed as *pressures that can support a certain sized column of mercury* (at a given elevation and temperature).

Standard atmospheric pressure (**1 atm**) is the pressure that supports a column of mercury **760 mm** high at 0°C at sea level.

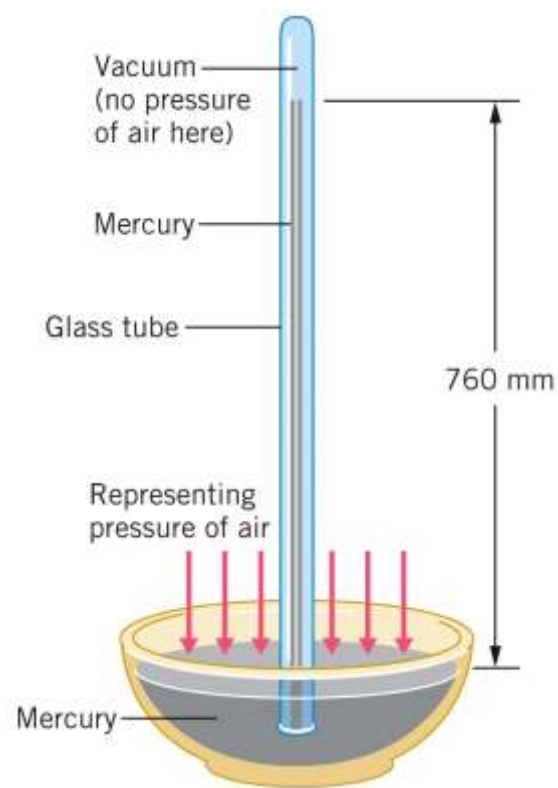
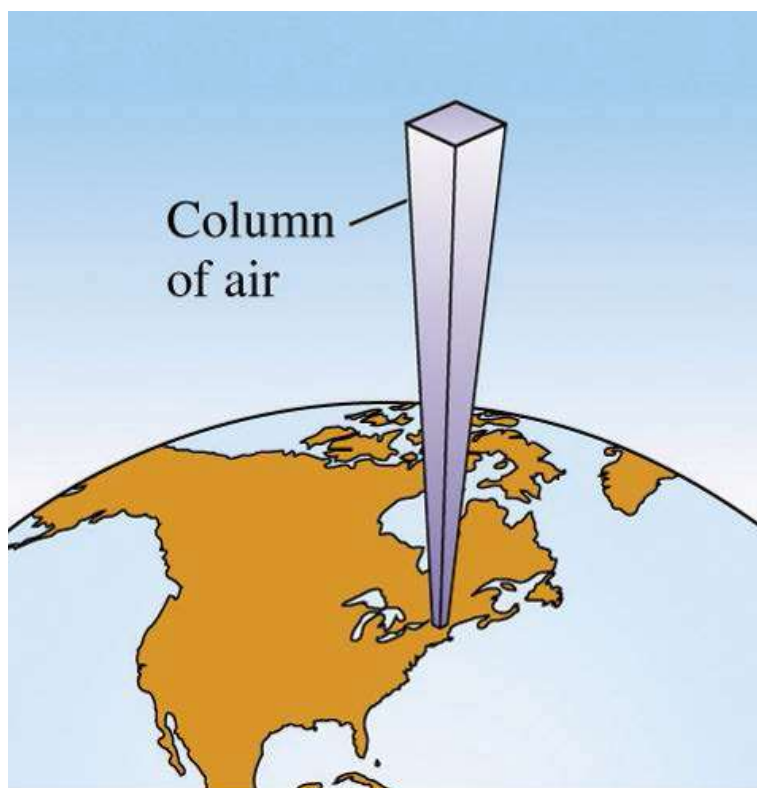
$$1 \text{ atm} = 760 \text{ mmHg} = 760 \text{ torr} = 1.01325 \times 10^5 \text{ Pa} = 101.325 \text{ kPa} = 29.92 \text{ inHg} = 14.696 \text{ psi}$$

$$1 \text{ torr} = 1 \text{ mmHg}$$

$$1 \text{ bar} = 10^5 \text{ Pa}$$

$$1 \text{ bar} \approx 1 \text{ atm.}$$

Named after Torricelli who invented the **barometer** - a barometer is an instrument that measures **atmospheric pressure**.

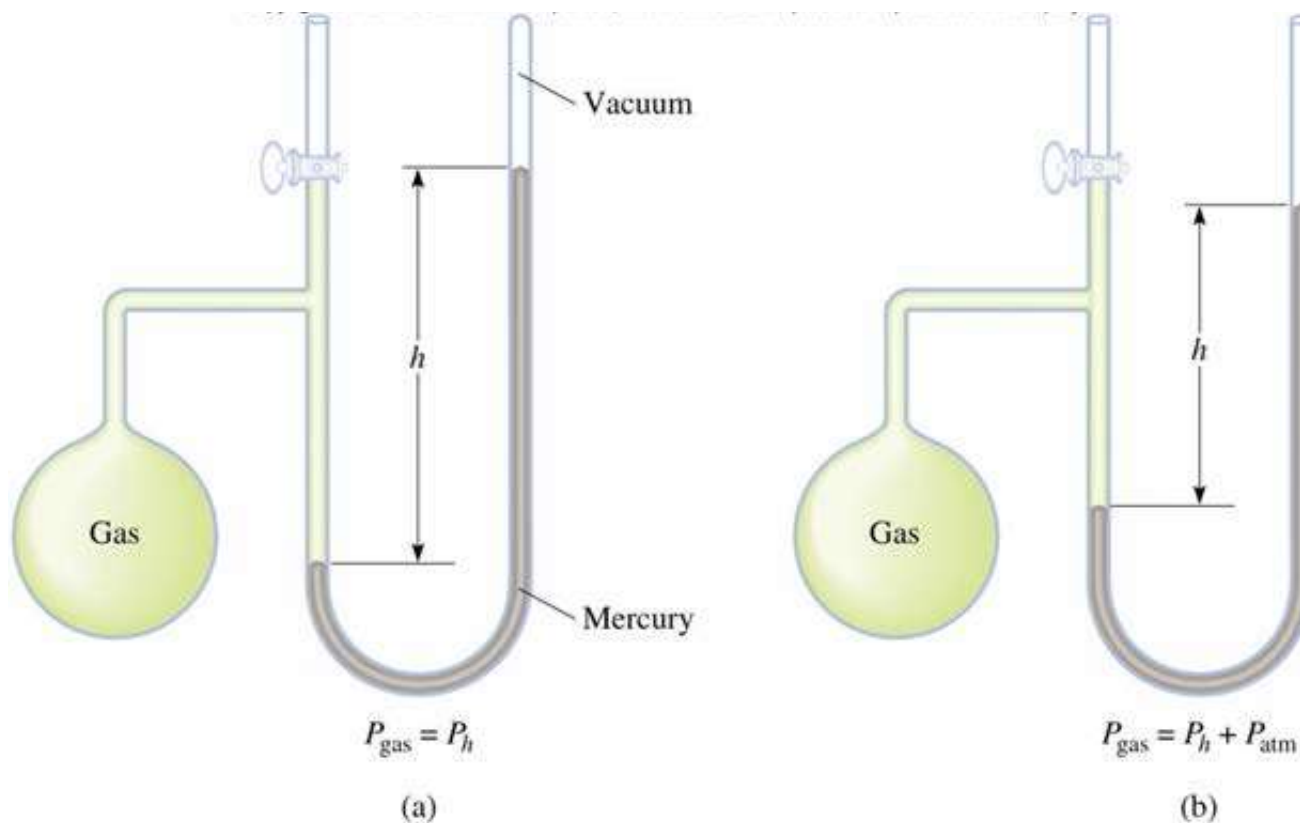


Mt Everest	29000 ft	253 mmHg	(low pressure)
Denver	5,690 ft	620 mmHg	
Dead Sea	1,407 ft below sea level	799 mmHg	(high pressure)

A **manometer** is an instrument that can measure pressure (of gases **other** than the atmosphere).

Either they are (a) **closed tube** (to measure pressure below atmospheric), or

(b) **open tube** (to measure pressure equal or greater than atmospheric pressure).



Mercury is used since it has such a *high density* (1.36 g/mL).

The Gas Laws

The **gas laws** were developed at the end of the 18th century, when scientists (through **experimental** observations) began to realize that relationships between the **pressure**, **volume** and **temperature** of a sample of gas could be obtained which would hold to a good approximation for **all** gases. Gases behave in a similar way over a wide variety of conditions because they all have *molecules* which are *widely spaced*.

Previously: *these four inter-related physical properties are **Pressure, Volume, Temperature and Amount**.*

Boyle's Law (the **Pressure/Volume** Relationship – the 1600's)

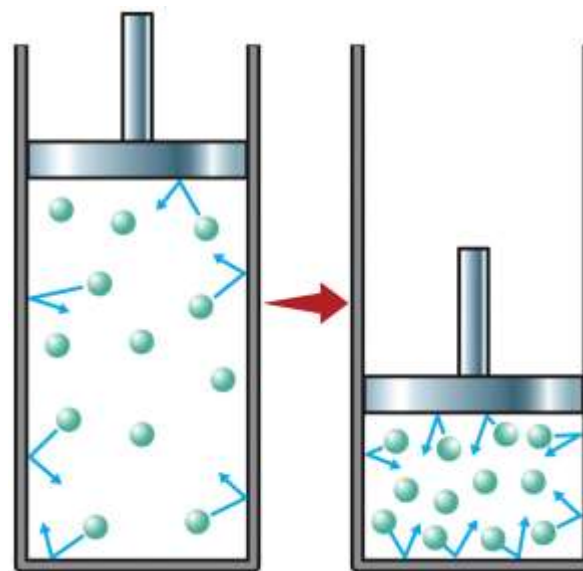
The **pressure** of a *fixed amount* of gas maintained at *constant temperature* is inversely proportional to the **volume**.

$$P \propto \frac{1}{V}$$

$$\text{Also: } P = k \times \frac{1}{V}$$

or

$$PV = k \quad \text{where } k = \text{constant.}$$



Smaller Volume \Rightarrow Larger Pressure

Charles's Law (the **Volume/Temperature** Relationship – in the 1700's).

The **volume** of a *fixed amount* of gas maintained at *constant pressure* is directly proportional to its absolute **temperature**.

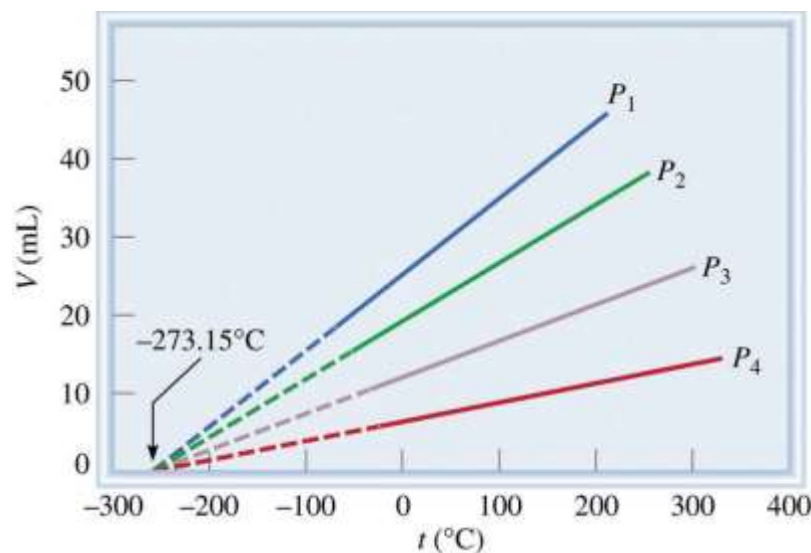
$$V \propto T$$

or

$$V = k \times T$$

or

$$\frac{V}{T} = k$$



At any pressure, the plot of **volume** versus **temperature** gave a **straight line**.

By extending the line to *zero volume*, every line gave the *same intercept* on the temperature axis.

In 1848, Kelvin identified this temperature as **absolute zero** (set as **0 K** on the absolute temperature scale), the **theoretically lowest attainable temperature**.

Gay-Lussac's Law (the **Pressure/Temperature** Relationship – in the 1800's).

The **pressure** of a *fixed amount* of gas maintained at *constant volume* is directly proportional to its absolute **temperature**.

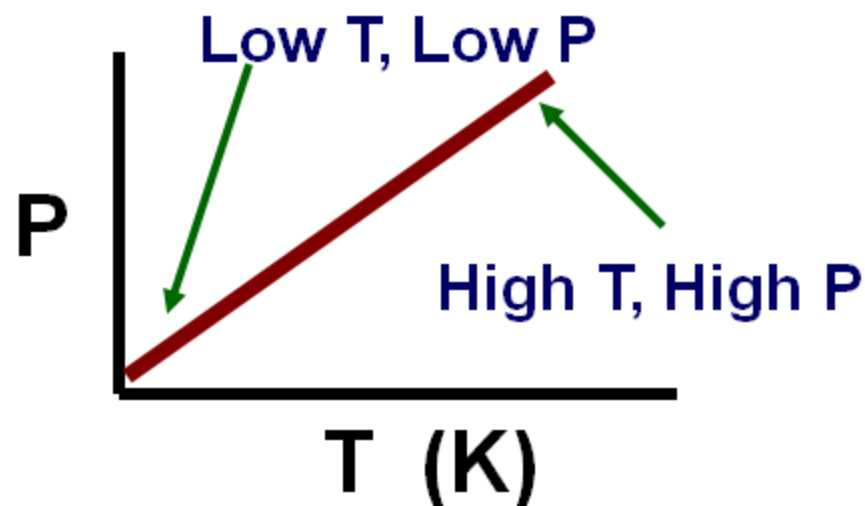
$$P \propto T$$

or

$$P = k \times T$$

or

$$\frac{P}{T} = k$$



Pressure *increases* as **temperature** *increases*.

Avogadro's Law (the **Volume/Amount** relationship - 1811)

At *constant pressure* and *temperature*, the **volume** of a gas is directly proportional to the **number of moles** of the gas present.

$$V \propto n \quad (\mathbf{n} = \text{amount of substance})$$

Or $V = k \times n$

So $\frac{V}{n} = k = V_m$ or $V = nV_m$

Where V_m is the molar volume = $22.4 \frac{\text{L}}{\text{mol}}$ (*more on this later*)

(**Equal volumes of gases** at the *same temperature* and *pressure* contain **equal numbers of molecules**).

The Ideal Gas Equation

Boyle's law (constant n and T) $V \propto \frac{1}{P}$

Charles's Law (constant n and P) $V \propto T$

Avogadro's Law (constant P and T) $V \propto n$

So if R is a (the Gas) constant: $V = R \frac{nT}{P}$

$$PV = nRT$$

Ideal Gas Law

An **ideal gas** is a *hypothetical* gas whose *pressure-volume-temperature behavior* can be completely accounted for by the **ideal gas equation**. (Ideal behavior is seen at **lower pressures** and **higher temperatures**).

For an **ideal** gas we pretend:

- Molecules of an ideal gas do **not attract** or **repel** one another.
- They have **negligible volume** compared to the container.

$PV=nRT$ is the **equation of state of a gas**.

If we know three of the 4 variables, we can calculate the fourth.

We can define the **state** of a gas by defining three of these values. (See Ch 6 in my notes for more on "states").

The Gas Constant

If we apply $PV=nRT$ at $0\text{ }^{\circ}\text{C}$ (273.15 K), using 1 mol of ideal gas occupying 22.4 L (*established by experiment*), we get the value of R:

$$R = 0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}$$

Beware of units – R is sometimes expressed as

$$R = 8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

Standard Temperature and Pressure (STP) is defined as:

STP

$$T = 273.15\text{ K} = 0\text{ }^{\circ}\text{C}$$

$$P = 1.0000\text{ atm}$$

All of the other gas laws can be derived from the ideal gas law...

So we have: $PV = nRT$ where R is a **constant**.

In Chemistry we often deal with *changes* or *modifications*:

$$R = \frac{P_1 V_1}{n_1 T_1} \text{ (before the change)} \quad \text{and} \quad R = \frac{P_2 V_2}{n_2 T_2} \text{ (after the change)}$$

Therefore: $\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}$ This is called the **Combined Gas Law**.

If the number of moles doesn't change (common for gas experiments, $n_1 = n_2$)

then: $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

If other variables are constant we get these useful forms:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \qquad \frac{V_1}{T_1} = \frac{V_2}{T_2} \qquad P_1 V_1 = P_2 V_2$$

Problem: An inflated balloon has a volume of 6.0 L at sea level (1.0 atm) and is allowed to ascend in altitude until the pressure is 0.45 atm. During the ascent the temperature of the gas falls from 22 °C to -21 °C.

Calculate the volume of the balloon at its final altitude.

So we know:

$$V_1 = 6.0 \text{ L}$$

$$V_2 = ?$$

$$P_1 = 1.0 \text{ atm}$$

$$P_2 = 0.45 \text{ atm}$$

$$T_1 = 22 \text{ }^\circ\text{C}$$

$$T_2 = -21 \text{ }^\circ\text{C}$$

Use KELVINS in Gas problems!

$$T_1 = 295 \text{ K}$$

$$T_2 = 252 \text{ K}$$

$$\begin{aligned} \frac{P_1 V_1}{T_1} &= \frac{P_2 V_2}{T_2} & \text{so} & \quad V_2 = \frac{P_1 V_1 T_2}{T_1 P_2} \\ & & & = \frac{(1.0 \text{ atm})(6.0 \text{ L})(252 \text{ K})}{(295 \text{ K})(0.45 \text{ atm})} & = 11.4 \text{ L} \\ & & & & = 11. \text{ L} \end{aligned}$$

Problem: Calculate the volume occupied by 0.54 mol of N₂ at 15 °C and 0.976 atm.

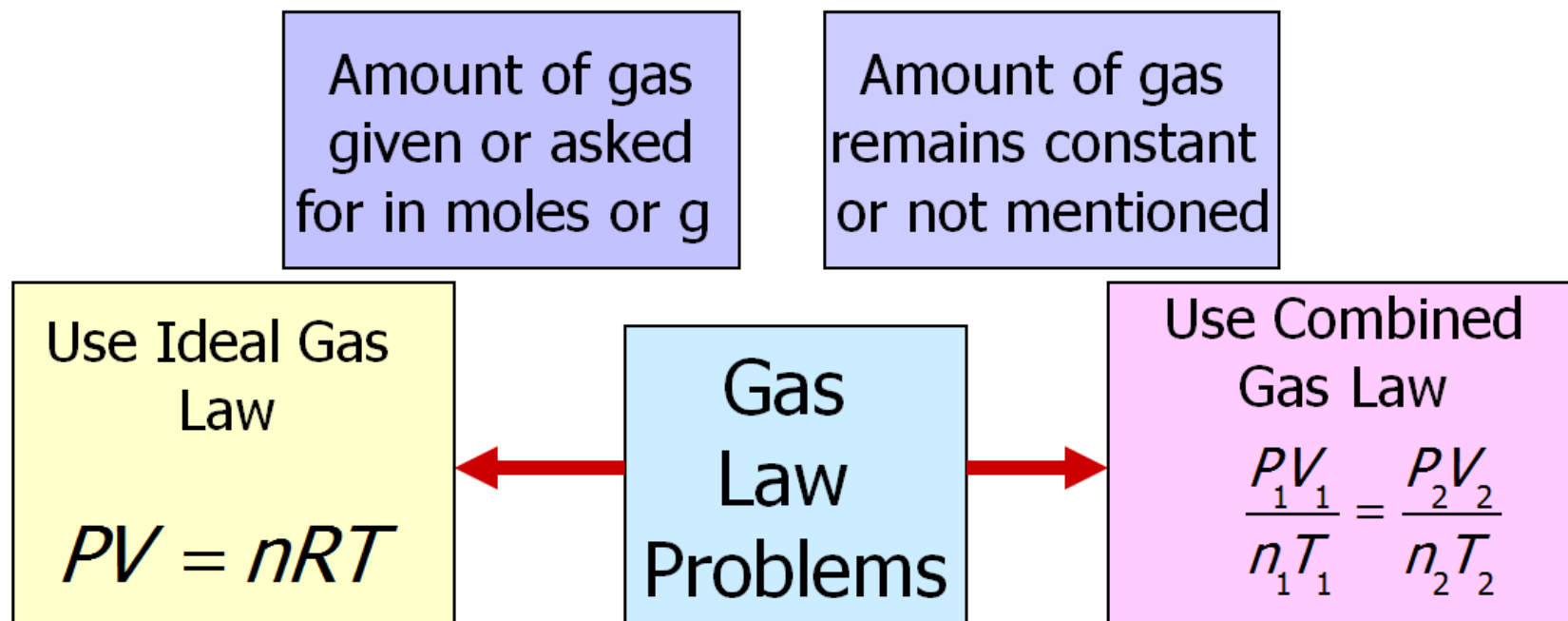
If given moles, use the ideal-gas law: $PV = nRT$

$$V = \frac{nRT}{P} = \frac{(0.54 \text{ mol}) \left(0.08206 \frac{\text{L atm}}{\text{mol K}}\right) (288 \text{ K})}{(0.976 \text{ atm})}$$

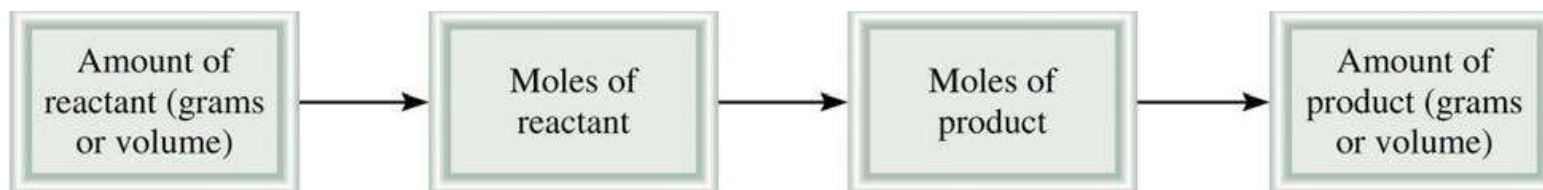
15 °C = 288 K
|

$$= 13. \text{ L}$$

When to use the [Ideal Gas Law](#), or the [Combined Gas Law](#) ?

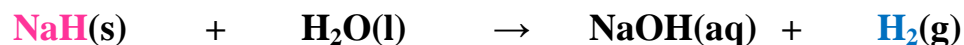


Stoichiometry: Stoichiometric connections can be included in gas law type problems:



Problem: What is the pressure in atmospheres in a 35.0 L balloon at 25.0 °C filled with dried hydrogen gas produced by the reaction of 39.8 g of NaH with water?

We need to find the number of moles of hydrogen from the *balanced* equation:



$$\begin{aligned} \text{Molar Mass NaH} &= 22.99 + 1.01 \\ &= 24.00 \text{ g/mol} \end{aligned}$$

$$39.8 \text{ g NaH} \times \frac{1 \text{ mol NaH}}{24.00 \text{ g NaH}} \times \frac{1 \text{ mol H}_2}{1 \text{ mol NaH}} = 1.66 \text{ mol H}_2$$

Moles of NaH
Moles of H₂

So put that into:

$$P = \frac{nRT}{V} = \frac{(1.66 \text{ mol}) (0.08206 \frac{\text{L atm}}{\text{mol K}}) (298 \text{ K})}{(35.0 \text{ L})} = 1.16 \text{ atm}$$

25 °C = 298 K

Further Applications of the Ideal-Gas Equation (to determine **molecular weights**)

$$\frac{n}{V} = \frac{P}{RT} \quad \text{if we multiply both sides by the Molecular Weight, } M, \text{ of the gas:}$$

$$\frac{nM}{V} = \frac{PM}{RT} \quad \text{but } \frac{nM}{V} = \frac{\text{moles}}{\text{liter}} \cdot \frac{\text{grams}}{\text{mole}} = \frac{\text{grams}}{\text{liter}} = \text{density (of a gas), } d$$

$$d = \frac{PM}{RT} \quad \text{rearranged is } M = \frac{dRT}{P}$$

Problem: If a 2.00 L flask contains 3.11 g of cyclopropane gas at 684 torr and 23.0 °C, what is the molecular weight of cyclopropane? ($R = 0.08206 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}$)

$$M = \frac{dRT}{P} = \frac{\left(\frac{3.11 \text{ g}}{2.00 \text{ L}}\right) (0.08206 \frac{\text{L atm}}{\text{mol K}}) (296 \text{ K})}{\left(684 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}}\right)} = 42.0 \frac{\text{g}}{\text{mol}}$$

23 °C = 296 K

Convert P from torr to atm

An alternative solution could find the number of *moles*, and then use that to find the MW:

Convert P from torr to atm

$$n = \frac{PV}{RT} = \frac{\left(684 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} \right) (2.00 \text{ L})}{\left(0.08206 \frac{\text{L atm}}{\text{mol K}} \right) (296 \text{ K})} = 0.0741 \text{ mol}$$

23 °C = 296 K

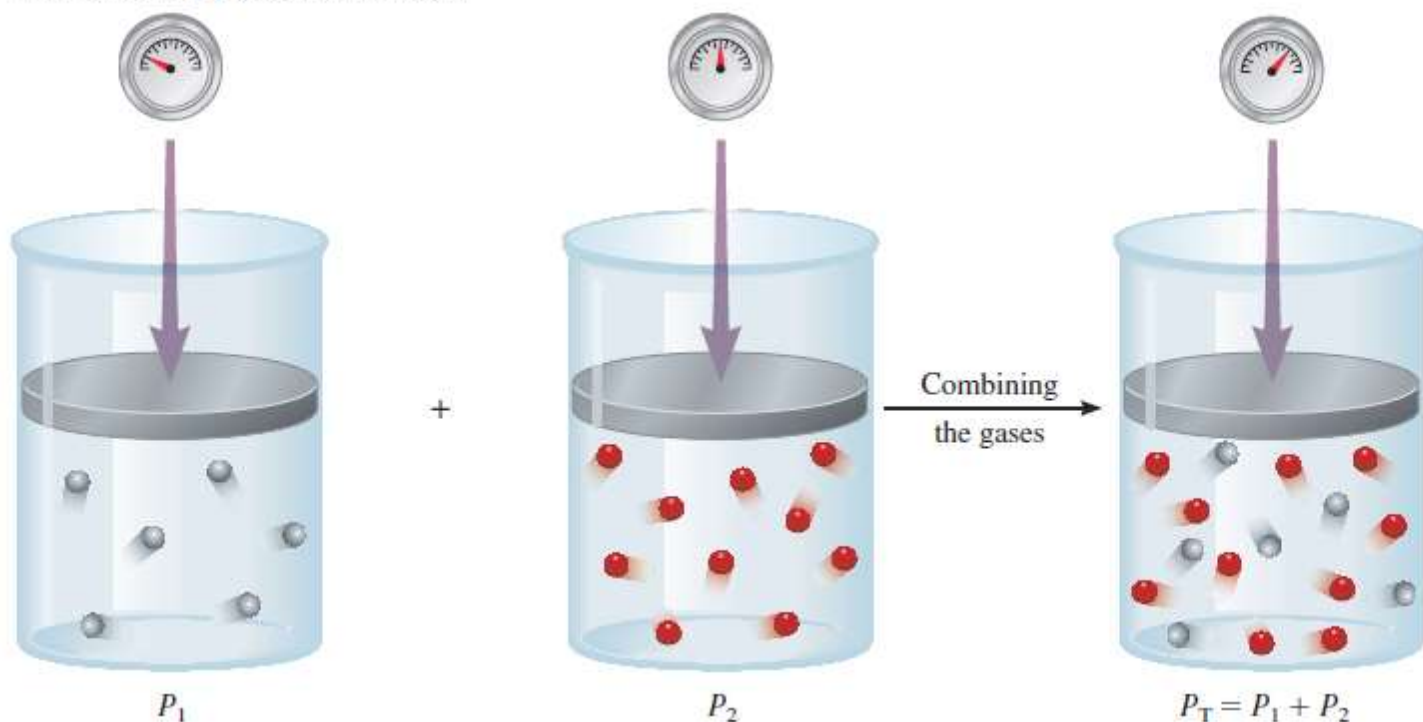
$$\text{Molar mass} = \frac{3.11 \text{ g}}{0.0741 \text{ mol}} = 42.0 \frac{\text{g}}{\text{mol}}$$

Gas Mixtures and Partial Pressures

So far we have talked about **pure** gaseous substances – but in reality we will encounter **mixtures** of gases.

Dalton's Law of Partial Pressures (1801) – the **total pressure** of a **mixture** of (*non-reacting*) gases equals the **sum** of the **pressures** that **each** would exert if it were present alone.

Volume and temperature are constant



The **total** pressure is the same as the *sum* of the grey pressure *and* the red pressure.

We can express this [mathematically](#):

(Assuming each gas behaves *ideally*)

$$P_{total} = P_1 + P_2 + P_3 + \dots$$

$$P_{total} = (n_1 + n_2 + n_3 + \dots) \frac{RT}{V} = n_{total} \left(\frac{RT}{V} \right)$$

$$\frac{P_1}{P_{total}} = \frac{n_1 RT/V}{n_{total} RT/V} = \frac{n_1}{n_{total}}$$

The mole fraction of gas 1: $X_1 = \frac{n_1}{n_{total}}$

$$\sum X_i = X_1 + X_2 + X_3 + \dots = 1$$

$$P_1 = \left(\frac{n_1}{n_{total}} \right) P_{total} = X_1 P_{total}$$

X_i is the [mole fraction](#) of i, which is a dimensionless quantity that expresses the *ratio* of the *number of moles* of [one component](#) to the **total number of moles** of [all the components](#) present.

Sometimes [mole fraction](#) is also expressed as [Mole Percent](#):

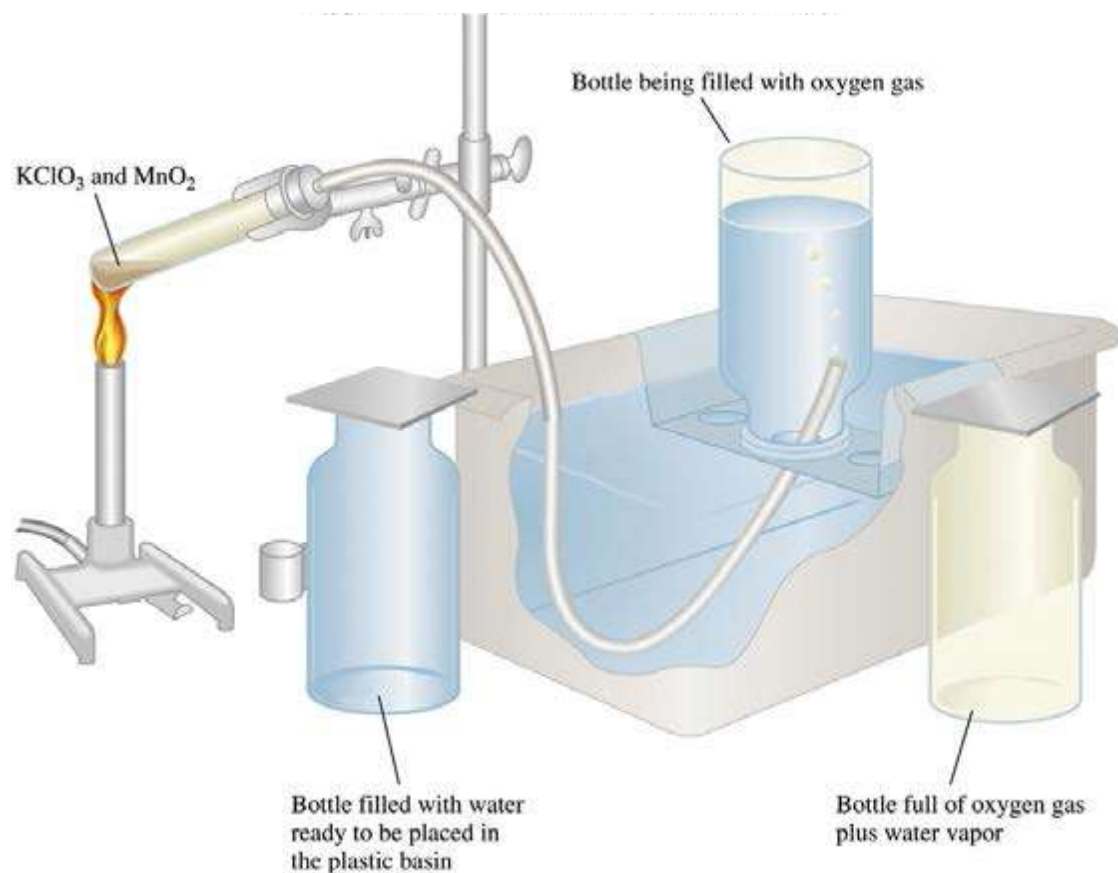
$$\text{Mole \%} = X_a \times 100\%$$

$$X_a = \frac{1}{2} \quad \Rightarrow \quad \text{mole percent} = 50\%.$$

This is useful for gases collected over water. E.g. If oxygen is collected over water, then the total pressure is:

$$P_{total} = P_{O_2} + P_{H_2O}$$

The pressure of gas in the bottle is not only due to O_2 , but also to water vapor. The vapor pressure of water varies with temperature. If we are to calibrate the bottle (for amount of O_2 produced), we must take this into account.



Pressure of Water Vapor at Various Temperatures

Temperature (°C)	Water Vapor Pressure (mmHg)
0	4.58
5	6.54
10	9.21
15	12.79
20	17.54
25	23.76
30	31.82
35	42.18
40	55.32
45	71.88
50	92.51
55	118.04
60	149.38
65	187.54
70	233.7
75	289.1
80	355.1
85	433.6
90	525.76
95	633.90
100	760.00

Problem: A mixture of gases contains 0.75 mol N₂, 0.30 mol O₂, and 0.15 mol CO₂.

If the total pressure is 1.56 atm, what is the partial pressure of each component?

$$X_{N_2} = \frac{n_{N_2}}{n_{\text{total}}} = \frac{0.75 \text{ mol}}{1.20 \text{ mol}} = 0.625$$

$n_{\text{total}} = 0.75 + 0.30 + 0.15$
 $= 1.20 \text{ mol}$

$$X_{O_2} = \frac{n_{O_2}}{n_{\text{total}}} = \frac{0.30 \text{ mol}}{1.20 \text{ mol}} = 0.25$$

$$X_{CO_2} = \frac{n_{CO_2}}{n_{\text{total}}} = \frac{0.15 \text{ mol}}{1.20 \text{ mol}} = 0.125$$

Check $\Sigma = 1$

$$P_{N_2} = X_{N_2} P_{\text{total}} = (0.625) (1.56 \text{ atm}) = 0.98 \text{ atm}$$

$$P_{O_2} = X_{O_2} P_{\text{total}} = (0.25) (1.56 \text{ atm}) = 0.39 \text{ atm}$$

$$P_{CO_2} = X_{CO_2} P_{\text{total}} = (0.125) (1.56 \text{ atm}) = 0.20 \text{ atm}$$

Problem: At an underwater depth of 250 ft, the pressure is 8.38 atm. What should the mole percent of oxygen be in the diving gas for the partial pressure of oxygen in the mixture to be 0.21 atm, the same as in air at 1 atm?

$$\begin{aligned} P_{\text{O}_2} &= X_{\text{O}_2} P_{\text{total}} && \text{rearrange to give} && X_{\text{O}_2} &= \frac{P_{\text{O}_2}}{P_{\text{total}}} \\ &&& && &= \frac{0.21 \text{ atm}}{8.38 \text{ atm}} \\ &&& && &= 0.025 \end{aligned}$$

which as a mole percent = 2.5 %

Kinetic-Molecular Theory (Boltzmann and Maxwell – Late 1800's)

The **kinetic** (*molecular*) **theory** describes a gas as a large number of *submicroscopic particles* (atoms or molecules), all of which are in **constant, rapid motion** that have **randomness** arising from their many **collisions** with **each other** and with the **walls** of the **container**.

Kinetic theory explains **macroscopic** properties of gases, such as **pressure**, **temperature**, **viscosity**, **thermal conductivity**, and **volume**, by considering their *molecular composition* and *motion*.

The theory posits that gas **pressure** is due to the **impacts** on the **walls** of a **container**, of **molecules** or **atoms** moving at different *velocities*.

Assumptions made:

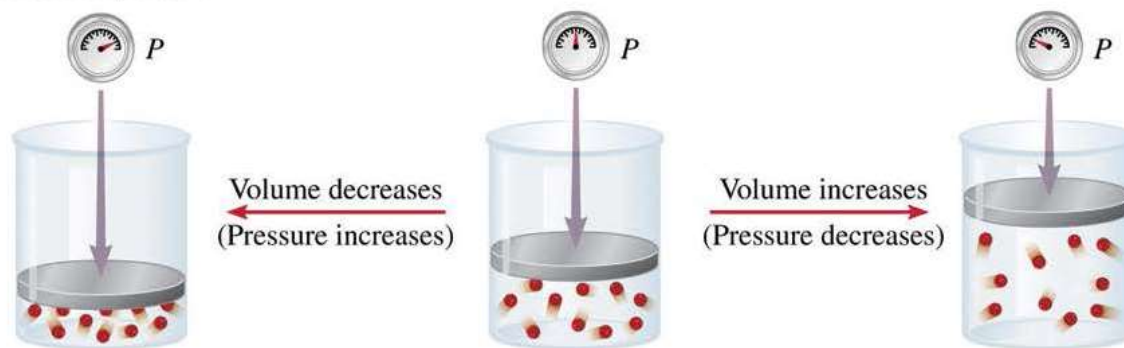
1. Gases are collections of **molecules** in *continuous random motion*.
2. Gas molecules are infinitesimally **small** particles.
3. Particles move in **straight lines** *until they collide*.
4. Molecules do **not** *influence* one another except when they *collide*.
5. The **average kinetic energy** of the molecules is **proportional** to the **absolute temperature**. (At any given **temperature** the **molecules** of all gases have the *same kinetic energy*).

Kinetic-Molecular Theory gives us an understanding of pressure and temperature on the molecular level.

- Pressure results from *collisions* of molecules with the walls of the container.
- The magnitude of pressure is determined by how often and how hard the molecules strike the walls of the container.
- Absolute temperature of a gas is a measure of the average kinetic energy of the molecules.
- Some molecules will have less kinetic energy and some will have more kinetic energy than the average (distribution).

Visual Illustrations

Increasing or decreasing the volume of a gas at a constant temperature



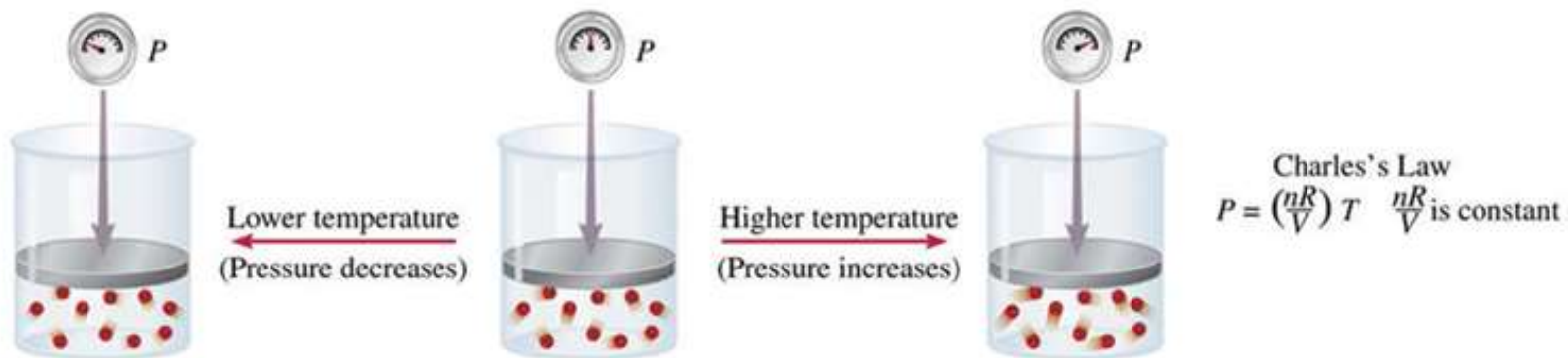
Boyle's Law

$$P = (nRT) \frac{1}{V} \quad nRT \text{ is constant}$$

More wall collisions = Higher P

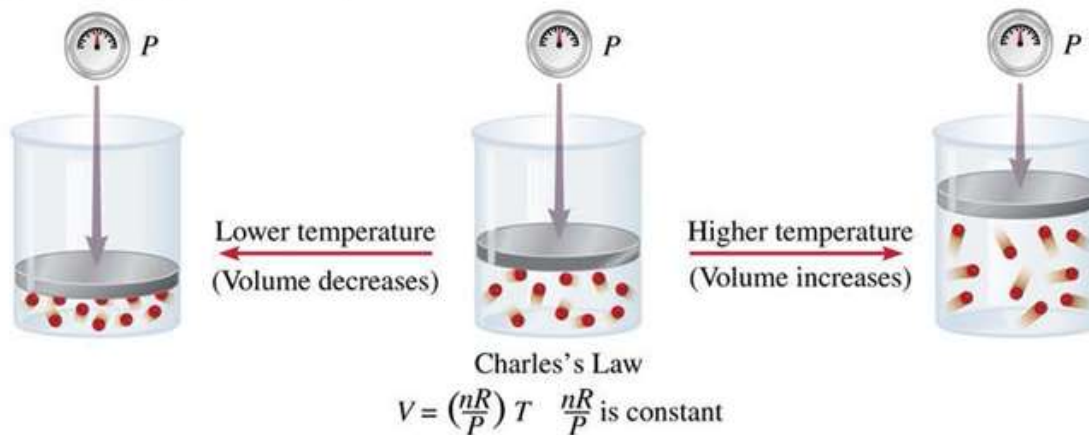
Less wall collisions = Lower P

Heating or cooling a gas at constant volume



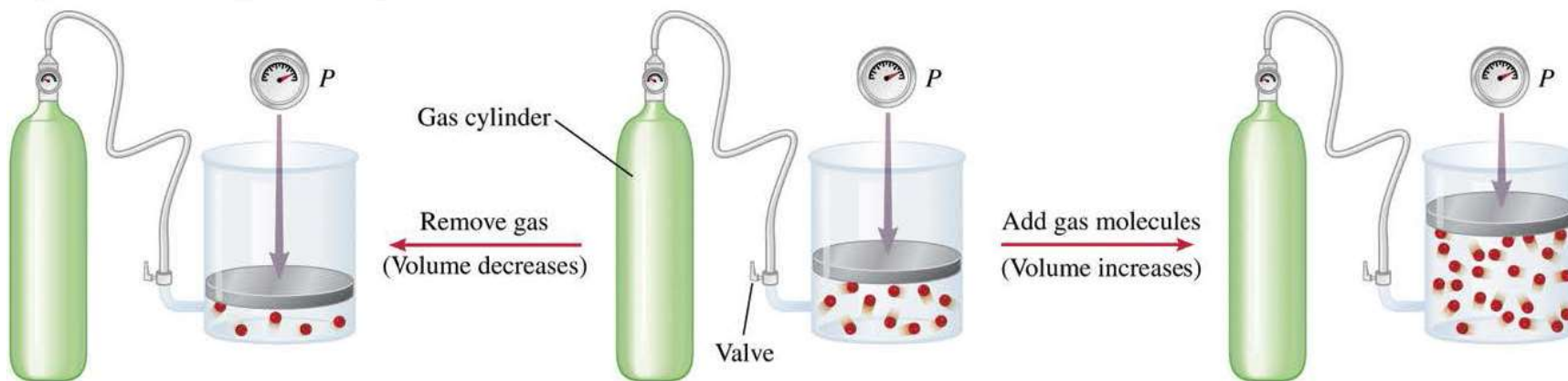
Lower T = slower motion (softer collisions) = Lower P Higher T = more ke = harder collisions = Higher P

Heating or cooling a gas at constant pressure



Lower T = slower motion, need smaller V to maintain P. Higher T = more motion, need larger V to keep P

Dependence of volume on amount
of gas at constant temperature and pressure



Avogadro's Law

$$V = \left(\frac{RT}{P}\right) n \quad \frac{RT}{P} \text{ is constant}$$

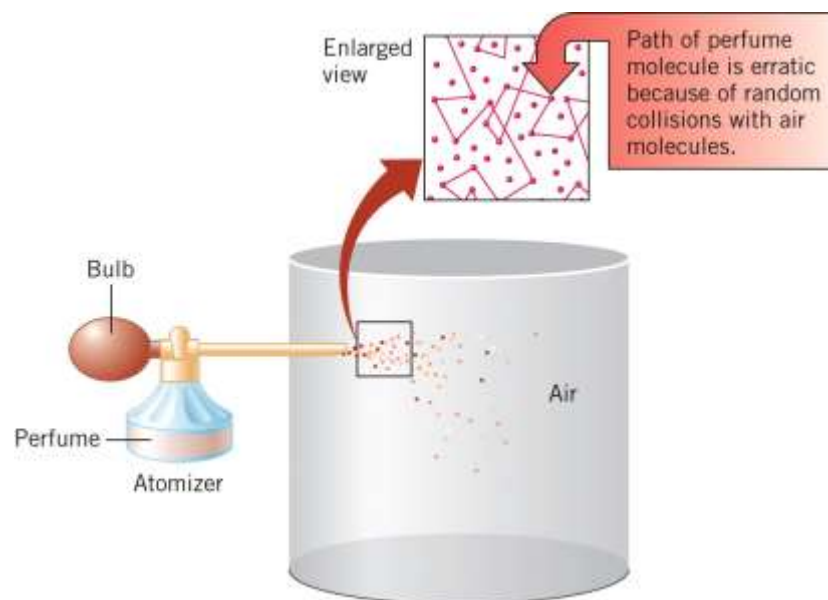
Less molecules means need smaller V to maintain P.

More molecules means need bigger V to keep P.

We now are able to address gaseous *motion*, and there are two different types: [diffusion](#) and [effusion](#)...

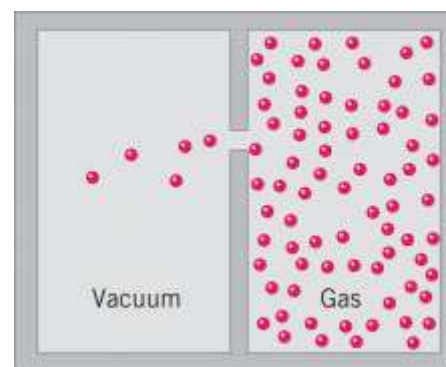
Diffusion is the *gradual mixing* of molecules of one gas with molecules of another, by virtue of their *kinetic properties*.

(E.g. smelling your food).



Effusion is the process by which a gas under pressure escapes from one compartment of a container to another by passing through a *small opening*.

Effusion is the process in which a gas escapes through a hole of diameter *considerably smaller* than the mean free path of the molecules.



(The **mean free path** is the average distance traveled by a gas molecule between collisions. At sea level, the mean free path for air molecules is about 6×10^{-6} cm).

Graham's Law of Effusion (1832)

Graham studied the rates of **effusion** (and **diffusion**) of gases, and their relationship to **molecular weight**.

He found that the rate of **effusion** is **inversely proportional** to the (*square root of the*) **molecular weight** of the gas.

$$\text{Rate of effusion} \propto \frac{1}{\sqrt{\text{molar mass}}} \quad \text{OR} \quad \text{Rate of effusion} \propto \frac{1}{\sqrt{M}}$$

$$\text{Average speed} \propto \frac{1}{\sqrt{\text{molar mass}}}$$

Graham's Law is usually used to compare the rates of effusion of two different gases:

For two gasses **A** and **B** (at the same Temperature and Pressure):

$$\frac{\text{rate of effusion of A}}{\text{rate of effusion of B}} = \frac{1/\sqrt{M_A}}{1/\sqrt{M_B}} = \sqrt{\frac{M_B}{M_A}}$$

$$\frac{\text{Time for A to effuse}}{\text{Time for B to effuse}} = \sqrt{\frac{M_A}{M_B}}$$

$$\frac{\text{rate of effusion of A}}{\text{rate of effusion of B}} = \frac{\text{time for B to effuse}}{\text{time for A to effuse}} = \sqrt{\frac{M_B}{M_A}}$$

The **rate of effusion** is the *number of molecules passing through a point in a given time*. The **longer** the time it takes, the **slower** is the rate. Therefore the **rate** is *inversely proportional* to the **time required** for effusion.

Distribution of Molecular Speeds

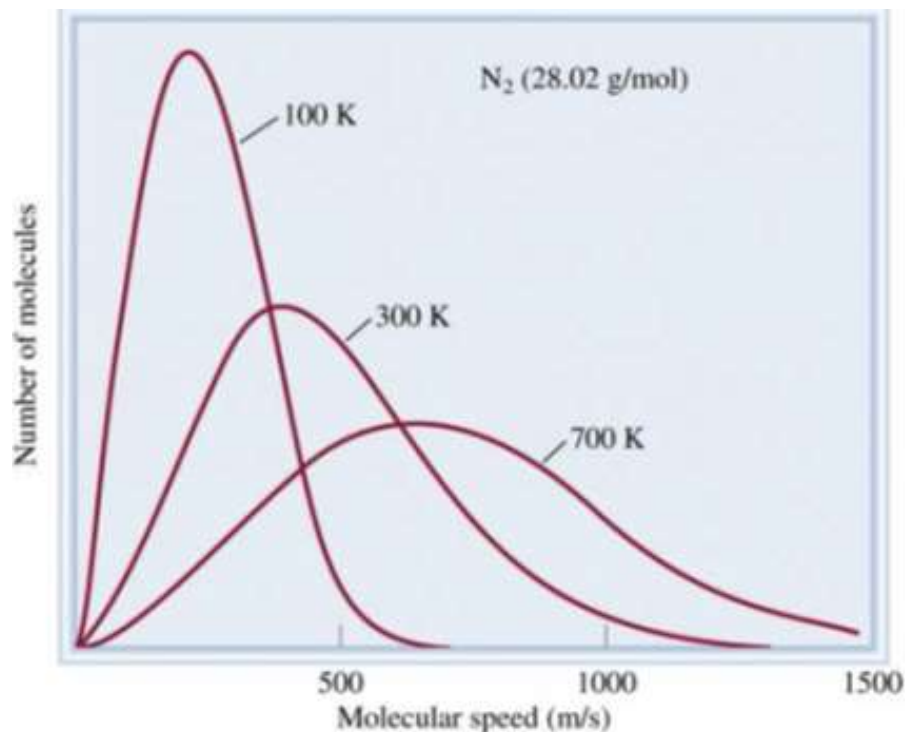
We previously said the **absolute temperature** of a gas is a measure of the **average kinetic energy** of the **molecules**, which is related to the **speed** of the molecules ($ke = \frac{1}{2}mv^2$).

This Maxwell speed distribution curve is for N_2 at three *different temperatures*, displaying the **number** of molecules moving at a certain **speed**.

The speed at the top of the curve is called the most *probable* speed because the largest number of molecules have that speed.

At lower temperatures, the molecules have less energy. Therefore, the speeds of the molecules are lower and the distribution has a **smaller range**.

As the temperature of the molecules increases, the distribution flattens out. Since the molecules have *greater energy* at **higher temperature**, the molecules are moving *faster*.

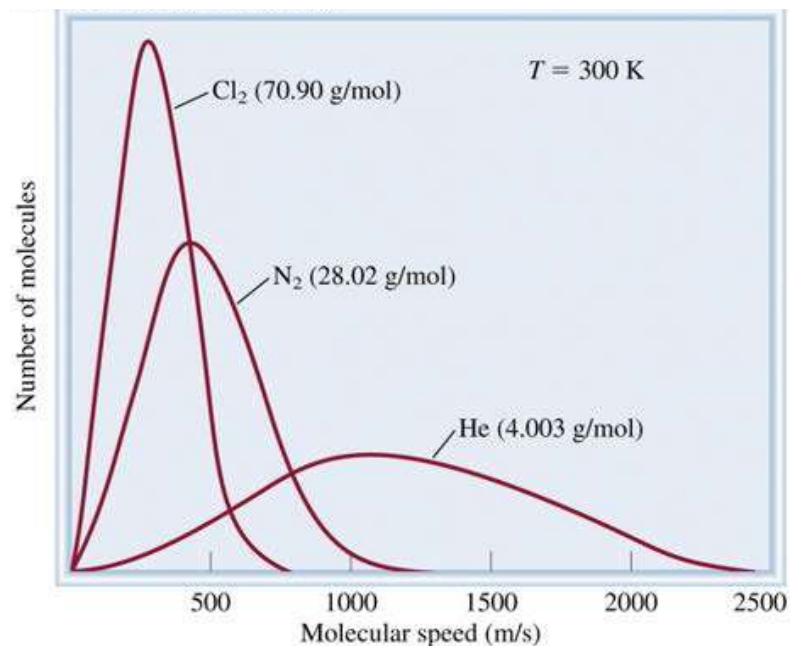


This graph shows the **speed** distribution of three *different* gases at the same temperature.

On average, **heavier** molecules move more **slowly** than **lighter** molecules.

(**Lighter** molecules move **faster**, on average, than **heavier** molecules).

Therefore, *heavier* molecules will have a *smaller* speed *distribution*, while **lighter** molecules will have a speed **distribution** that is more **spread out**.



Problem: Arsenic (III) sulfide sublimes readily. The molecules of the vapor phase are found to effuse through a tiny hole at 0.28 times the rate of effusion of Ar atoms under the same conditions of temperature and pressure. What is the molecular formula of arsenic (III) sulfide in the gas phase?

$$\begin{aligned}
 \frac{\text{Rate of effusion of A}}{\text{Rate of effusion of B}} &= \sqrt{\frac{M_B}{M_A}} \\
 \frac{1}{0.28} &= \sqrt{\frac{M_{\text{AS}}}{M_{\text{Ar}}}} = \sqrt{\frac{M_{\text{AS}}}{39.9}} \\
 &= (3.57)^2 \times 39.9 \\
 &= 508.5 \text{ g/mol} \\
 &= 510 \text{ g/mol (to 2 sig. figs.)}
 \end{aligned}$$

Arsenic Sulfide, "AS"
Argon

Since As = 74.9 and S = 32.1, $\text{As}_2\text{S}_3 = 246.1 \text{ g/mol}$

so it looks like in the gas phase it is *dimeric*, As_4S_6

Real Gases: Deviations from Ideal Behavior

Assumptions for Ideal Behavior included:

- Gas molecules do not exert forces, attractive or repulsive, on each other.
- The volume of the molecules is negligibly small compared with the volume of the container.

Ideal behavior is seen at **lower pressures** and **higher temperatures**.

But if we move away from these conditions, we observe that gases exhibit more **non-ideal** behavior at **higher pressures** and **lower temperatures**.

The **van der Waals equation** (or **van der Waals equation of state**, 1873) can be viewed as an adjustment to the ideal gas law that takes into account the **non-zero volume** of gas molecules, which are subject to an **inter-particle attraction**.

We know ideally that $\mathbf{PV} = \mathbf{nRT}$, but we can correct for **molecular attraction**, and **volume of molecules**:

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

a – magnitude of **a** reflects how strongly the gas molecules **attract** each other; has units of $\text{L}^2 \cdot \text{atm} / \text{mol}^2$

b – a measure of actual intrinsic **volume** occupied by a mole of gas molecules; has units of L / mol .