Chapter 6

Gases

Why study gases?

- To understand an important part of real world phenomena.
- A lot of industrial chemistry involves gases.
- They are the simplest of the three phases to understand and quantitatively model (i.e. predict) their behavior
- A good case study to see some scientific concepts and principles in action

A Gas

- Uniformly fills any container.
- Easily compressed.
- Mixes completely with any other gas.
- Exerts pressure on its surroundings.

Pressure

$$\text{Pressure} = \frac{\text{force}}{\text{area}}$$

SI units = Newton/meter^2 = 1 Pascal (symbol: Pa)

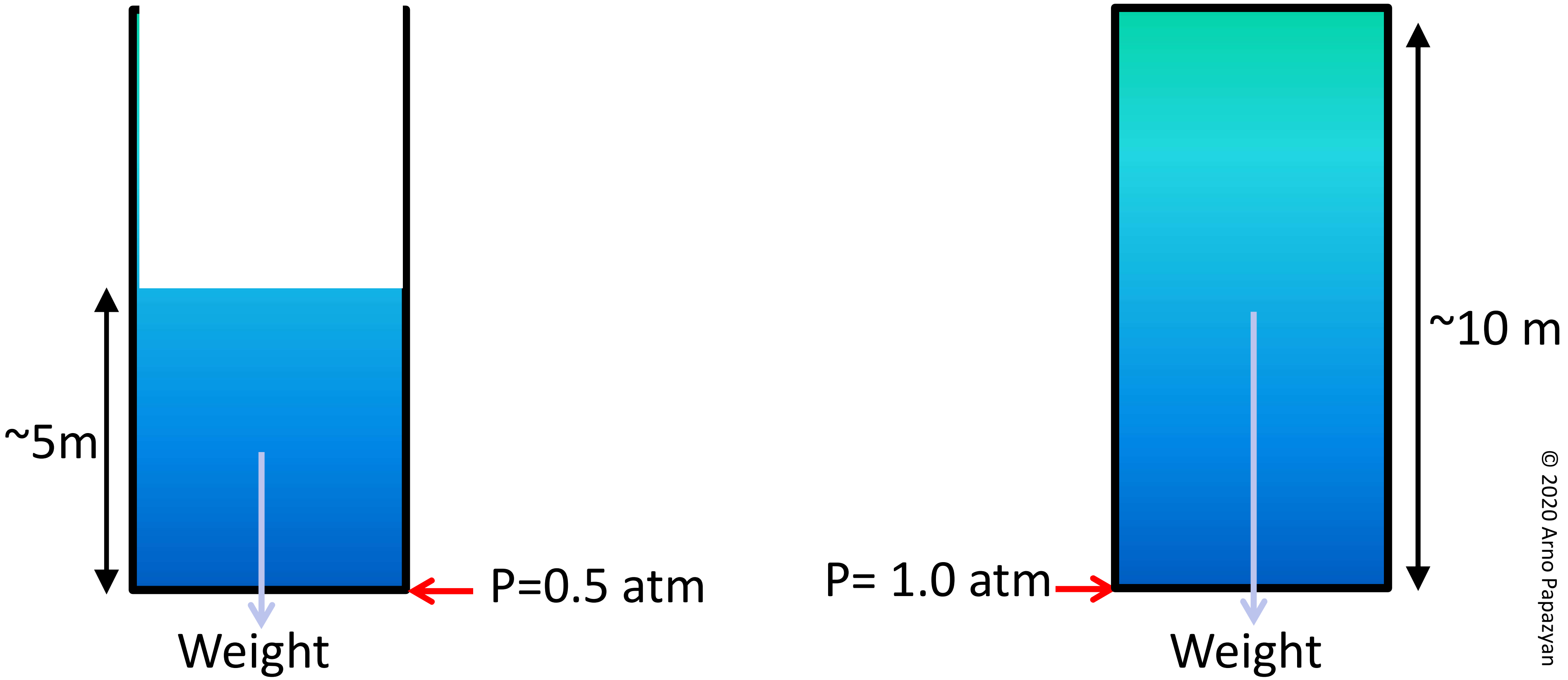
1 standard atmosphere (symbol: atm) = 101,325 Pa

1 standard atmosphere = 1 atm = 760 mm Hg = 760 torr

The “normal” atmospheric pressure is approximately equal to a “standard atmosphere” or simply “atmosphere”

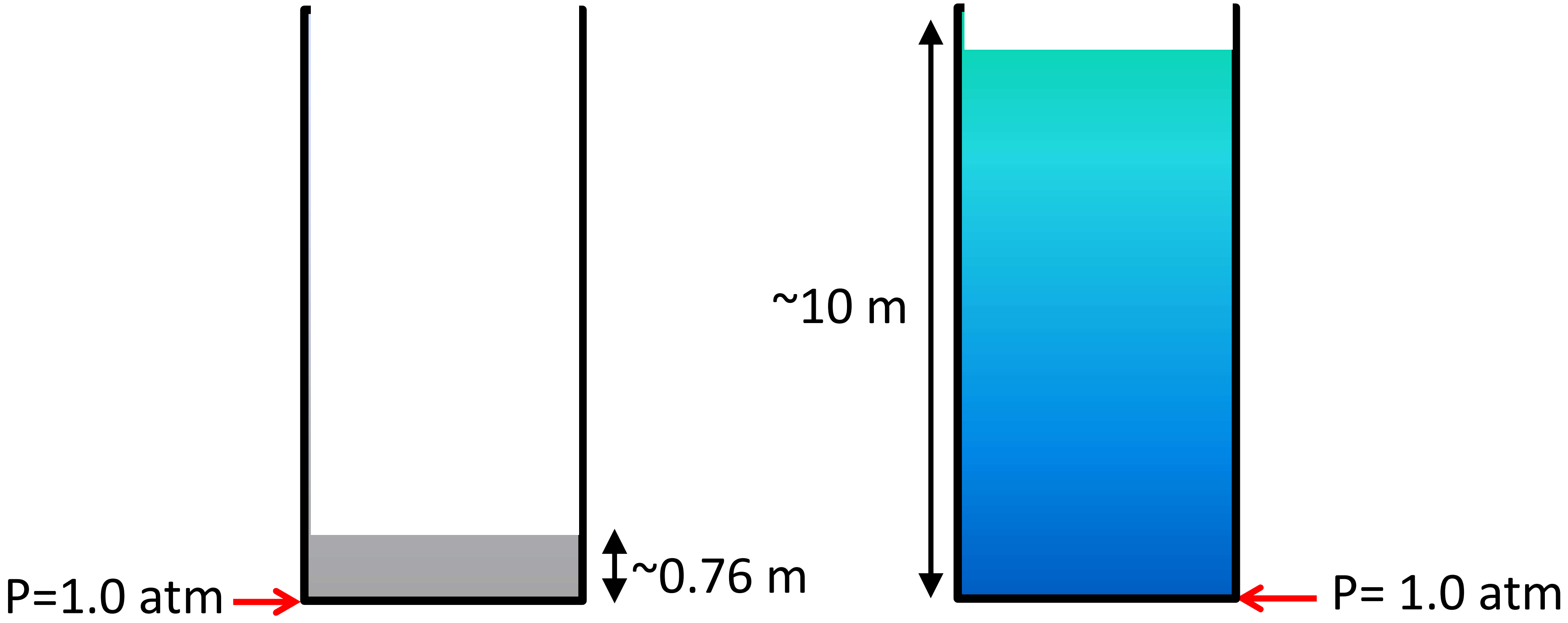
But first … let's understand how pressure is generated in dense materials (liquids and solids): by an external force

The weight of liquid "sitting" above an area generates hydrostatic pressure, which is literally the weight of the liquid column divided by the area on which it "sits"



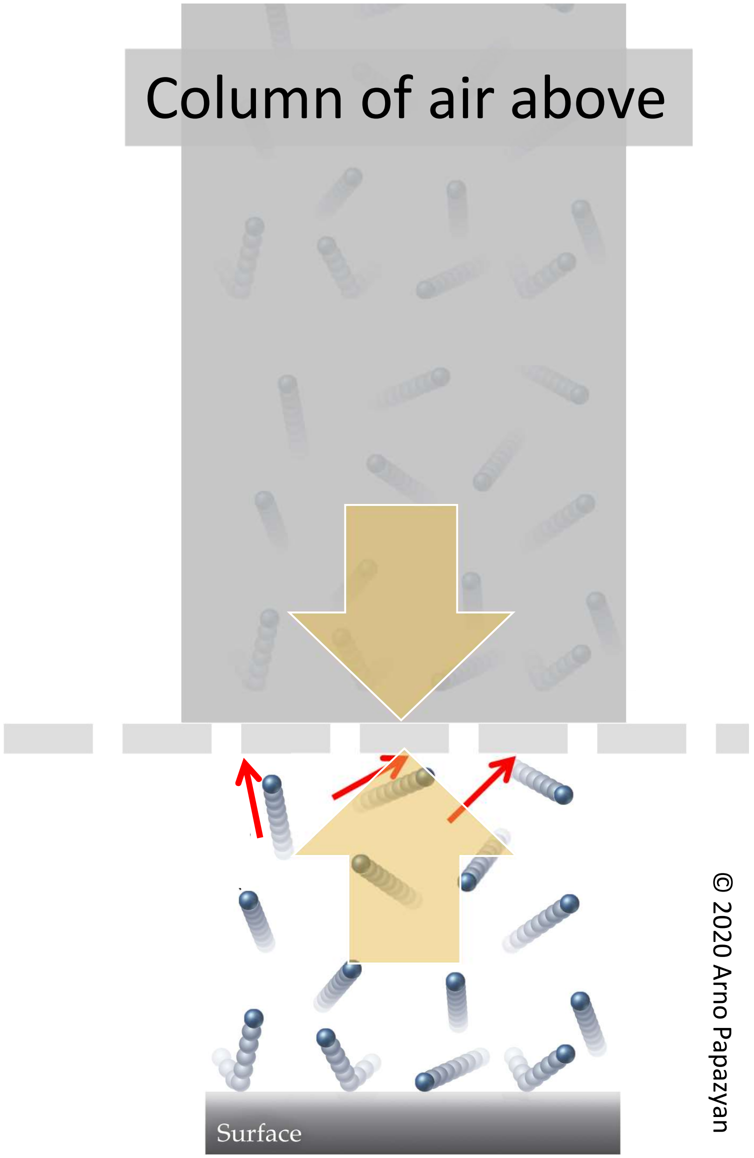
Dense liquids require less height to generate the same pressure as a less dense liquid

- Mercury is 13.6 denser than water
- 760 mm (0.760 m) generates the same hydrostatic pressure as ~10 m column of water



Normally, we can ignore the effect of gravity on the behavior of a human-scale sample of gas

But a planet-wide atmosphere is of course held in place and "compressed" to a pressure by gravity



Air around us is holding up the column of air above us in the atmosphere by applying a force in the opposite direction

So the air at the surface of the earth owes its pressure to the weight of the "column of air" sitting on top of any given point

But …

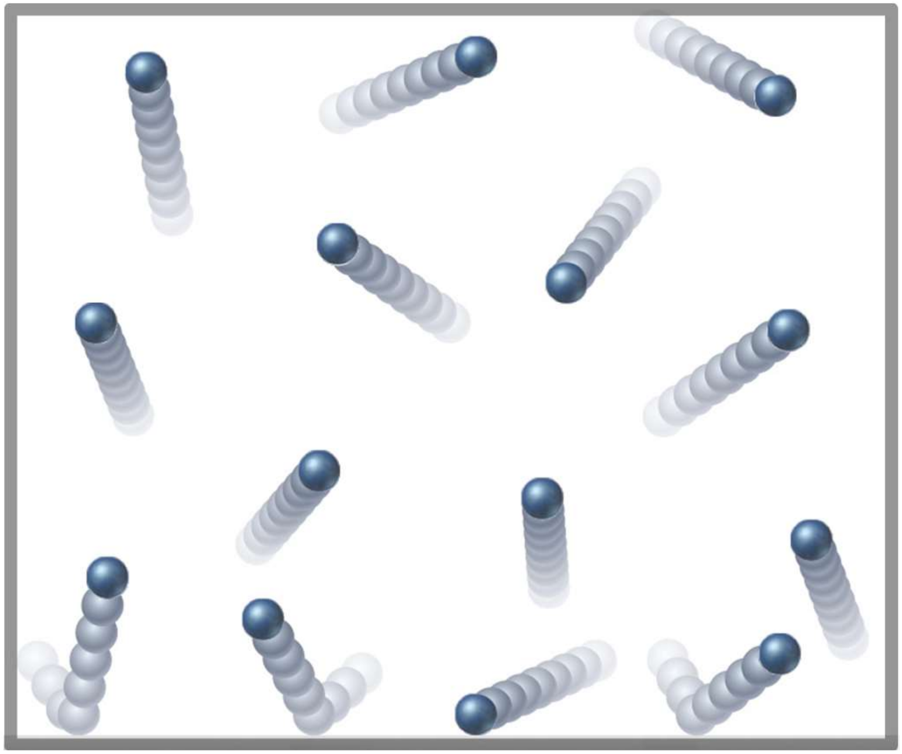
- What if we take a sample of the air and put it in a sealed box without altering its pressure?
- Will it have little or no pressure because there is no "column of air" above it?

No, it will generate the same pressure

- It will retain its pressure because the pressure of a **gas** is generated by its particles bouncing against the walls of its container.

We will **only** deal with human-scale samples where gravity is not important.

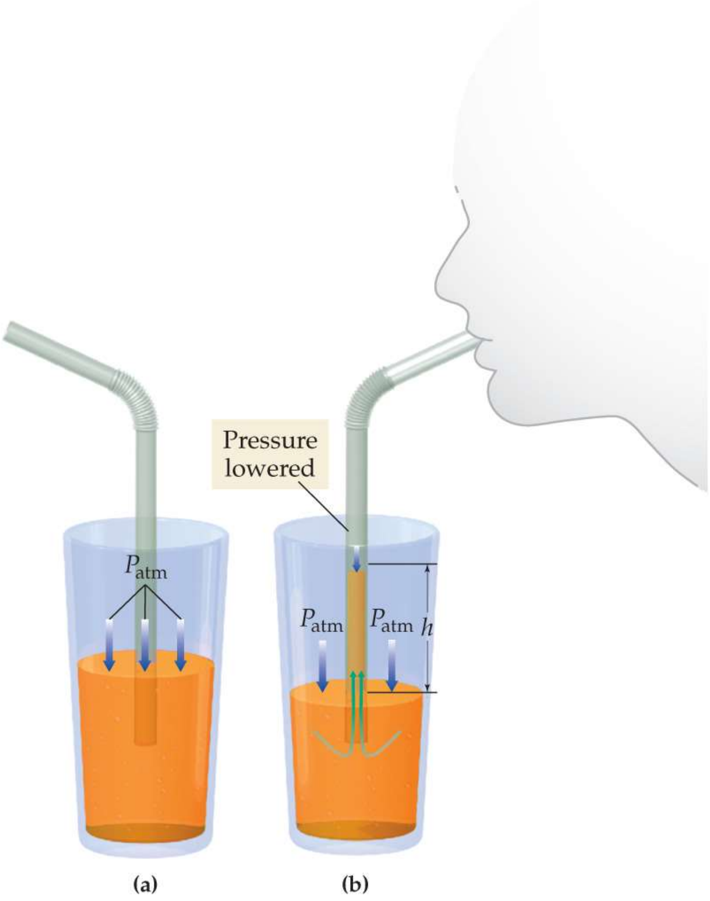
The gas will be contained within container walls.



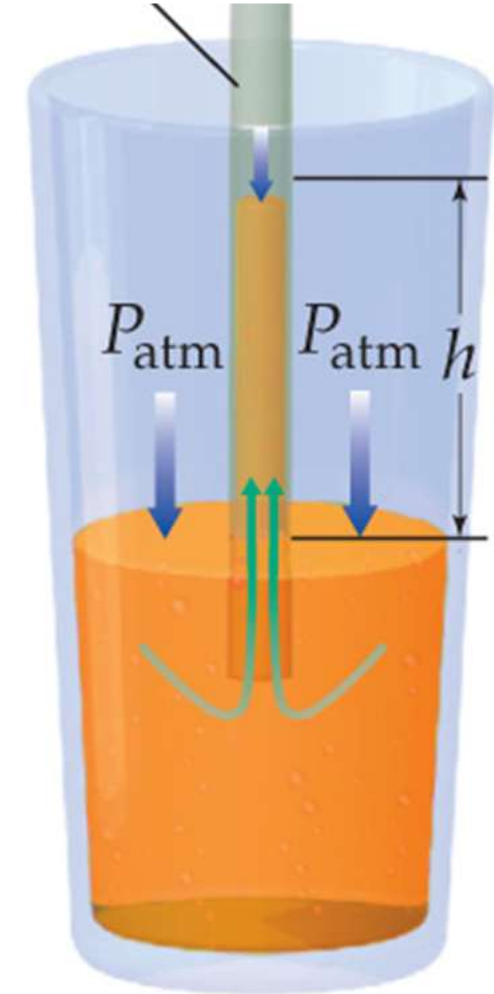
Heard of barometers? Let's first understand straws

(a) The pressure inside and outside the straw is the same, so the liquid levels inside and outside the straw are the same.

(b) When we suck on the straw, the pressure inside the straw is lowered. The greater pressure on the surface of the liquid <u>outside</u> the straw pushes the liquid up the straw.



Heard of barometers? Let's first understand straws

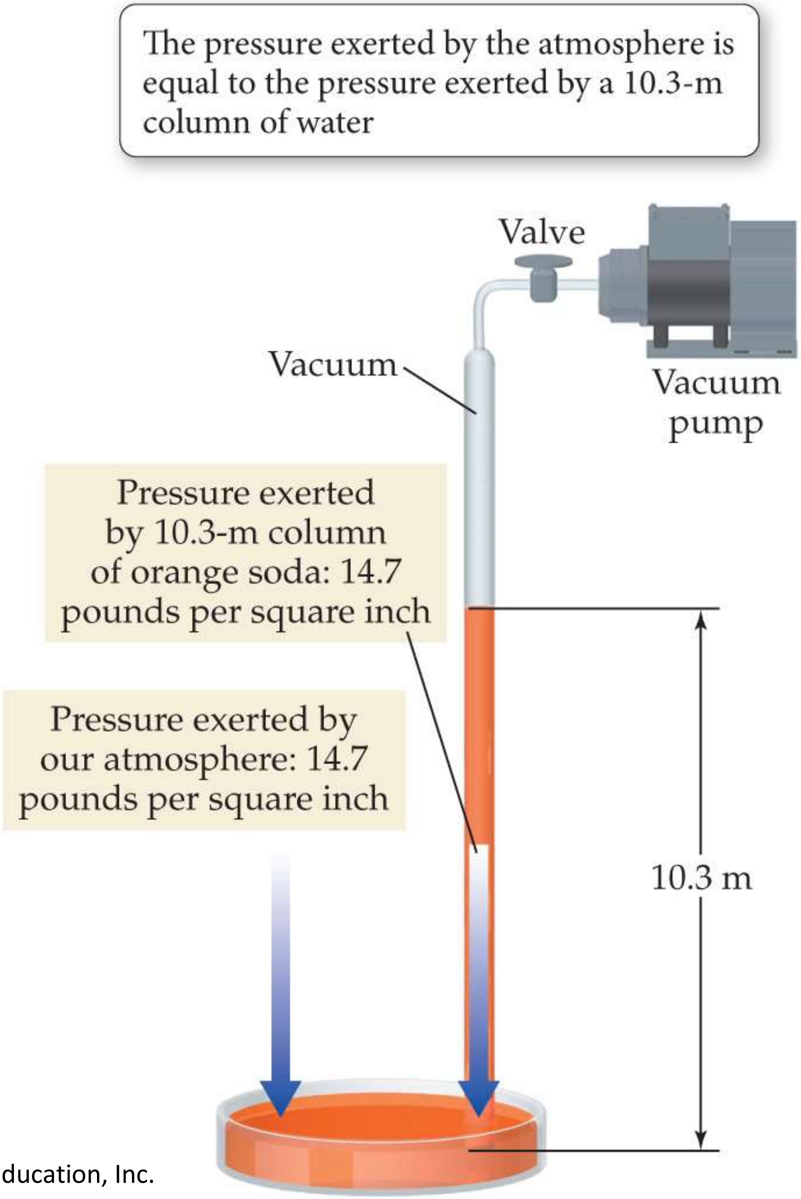


Note:

- Pressure is directionless
- If you apply it to a fluid, it is transmitted in all directions
- Atmosphere pressing "down" on the liquid surface translates to liquid pressing up into the straw

Heard of barometers? Let's first understand straws

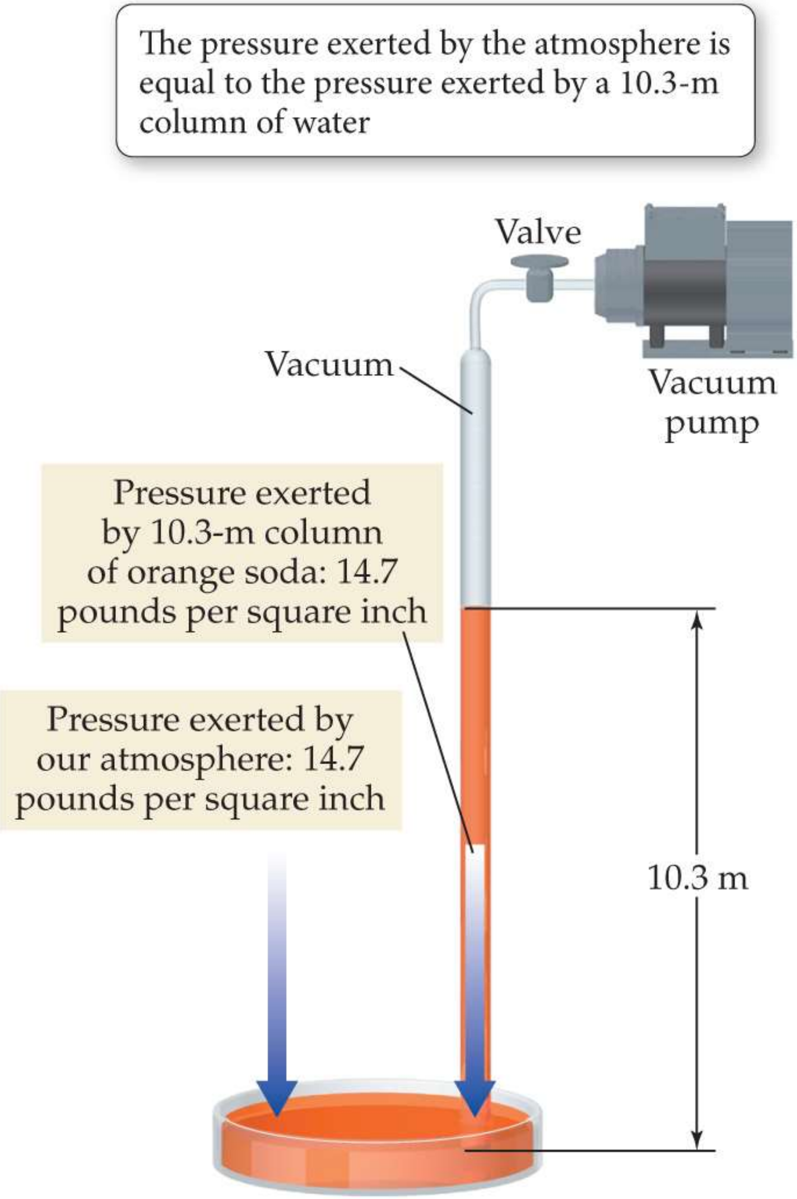
- Even if you formed a perfect vacuum with a pump, atmospheric pressure could only push orange soda to a total height of about 10 m.
- A column of water (or soda) 10.3 m high exerts the same pressure as the gas molecules in the atmosphere.



Heard of barometers? Let's first understand straws

- We could measure the height of the water column to measure the atmospheric pressure
- If the atmospheric pressure is holding up 10.342 meters, we could even make it a unit and say "atmospheric pressure is 10.342 meters water"
- But it would be a huge, unwieldy instrument
- **A much denser liquid would have much shorter height:**

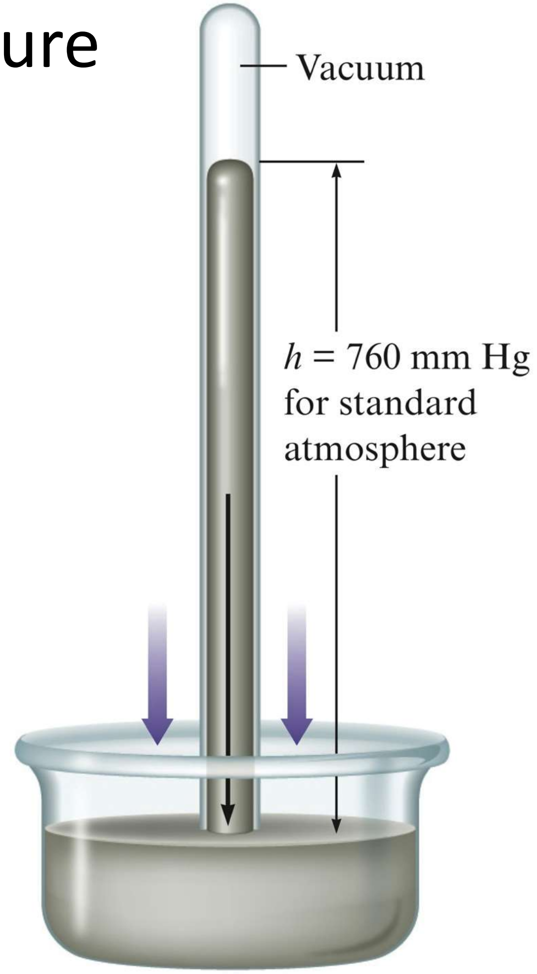
  Mercury!



Barometer

Device used to measure atmospheric pressure

Mercury flows out of the tube until the pressure of the column of mercury standing on the surface of the mercury in the dish is *equal* to the pressure of the air on the rest of the surface of the mercury in the dish.



Weight of the mercury column is balanced by the force due to air pressure

The width of the column doesn't matter. The wider it is, the heavier the column, but also the larger the force due to air pressure ($F=P\cdot A$)

Pressure unit conversions: An Example

The pressure of a gas is measured as 2.5 atm. Represent this pressure in both torr and pascals.

$$(2.5\ \cancel{\text{atm}})\times\left(\frac{760\ \text{torr}}{1\ \cancel{\text{atm}}}\right) = 1.9\times10^{3}\ \text{torr}$$

$$(2.5\ \cancel{\text{atm}})\times\left(\frac{101{,}325\ \text{Pa}}{1\ \cancel{\text{atm}}}\right) = 2.5\times10^{5}\ \text{Pa}$$

Gas Laws

Gas laws are mathematical relationships between the properties of a gas.

The **4 properties** (variables) that define the state of a gas are:

Pressure (**P**)

Volume (**V**)

Temperature (**T**) ← Must be in Kelvins! Cannot be in °C or °F!

Number of moles (**n**)

Liquid Nitrogen and a Balloon

Very cold: –320ºF (–196ºC)

Ken O'Donoghue

Ken O'Donoghue

Ken O'Donoghue

Liquid Nitrogen and a Balloon

What happened to the gas in the balloon?

- Lower temperature was accompanied by a lower volume of the gas in the balloon.

Liquid Nitrogen and a Balloon

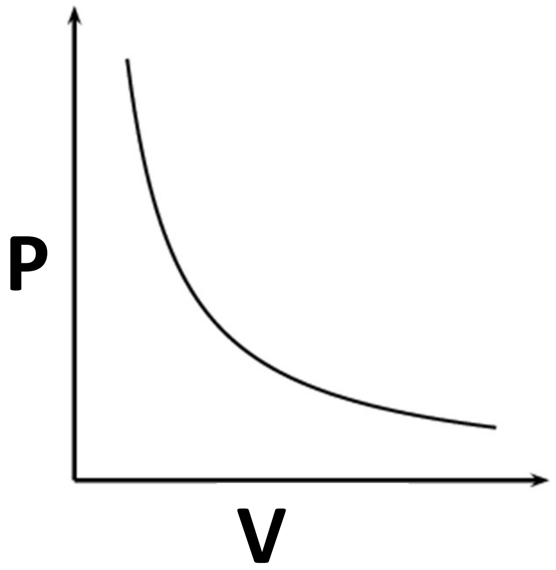
“Lower temperature was accompanied by a lower volume of the gas in the balloon” is an **observation** (a fact).

It does not yet rise to the level of a “law”

- But gas laws can be deduced from observations like these

Boyle's Law

At constant temperature (T) and moles (n) of gas, P and V are inversely proportional.



Which means:

$P \times V$ = [a constant value]

First state:

$P = P_1$ and $V = V_1$ ⇨ $P_1 \times V_1$ = [a constant]

Second state:

$P = P_2$ and $V = V_2$ ⇨ $P_2 \times V_2$ = [same constant]

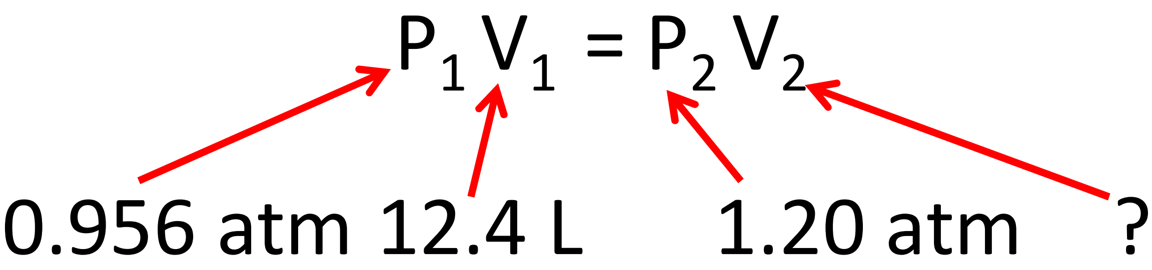
⇨ $P_1 \times V_1 = P_2 \times V_2$ Boyle's Law

Example:

A sample of helium gas occupies 12.4 L at 23˚C and 0.956 atm. What volume will it occupy at 1.20 atm assuming that the temperature stays constant?

We recognize this as a “Boyle’s Law” problem:

Temperature (T) is constant
Amount of gas (n) is constant (“a sample of gas”)
Pressure (P) and volume (V) are changing



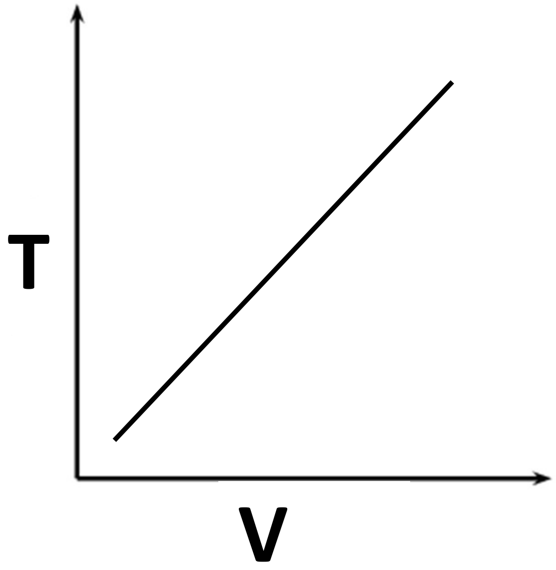
$$P_1 V_1 = P_2 V_2$$

0.956 atm 12.4 L 1.20 atm ?

$$(0.956)(12.4) = (1.20)\ V_2 \Longrightarrow V_2 = 9.88\ \mathrm{L}$$

Charles's Law

At constant pressure (P) and moles (n) of gas, V and T are directly proportional



Which means:

$$\frac{V}{T} = [\text{a constant value}]$$

First state:
$T = T_1$ and $V = V_1$ ⇨ $\frac{V_1}{T_1} = [\text{a constant}]$

Second state:
$T = T_2$ and $V = V_2$ ⇨ $\frac{V_2}{T_2} = [\text{same constant}]$

⇨

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

Charles's Law

In gas laws, **temperature unit must be Kelvin.**

You cannot use °C or °F !

Using use °C or °F would bring addition or subtraction into the equations, and the simple, direct or inverse proportionality relationships would be lost.

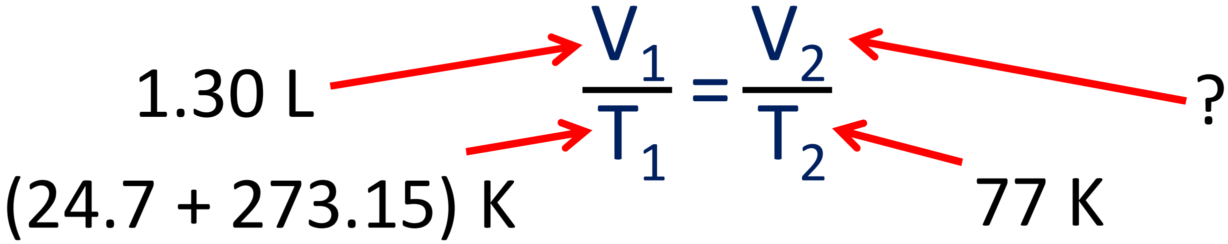
The gas laws that we learn would not apply if we use the wrong temperature unit!

Example:

A balloon containing 1.30 L of air at 24.7˚C is placed into a beaker containing liquid nitrogen at 77.0 kelvins. What will the volume of the sample of air become?

We recognize this as a "Charles's Law" problem:

- Pressure (P) is constant (for a balloon $P = P_{room}$)
- Amount of gas (n) is constant ("the sample of air")
- Temperature (T) and volume (V) are changing



1.30 L

(24.7 + 273.15) K

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

?

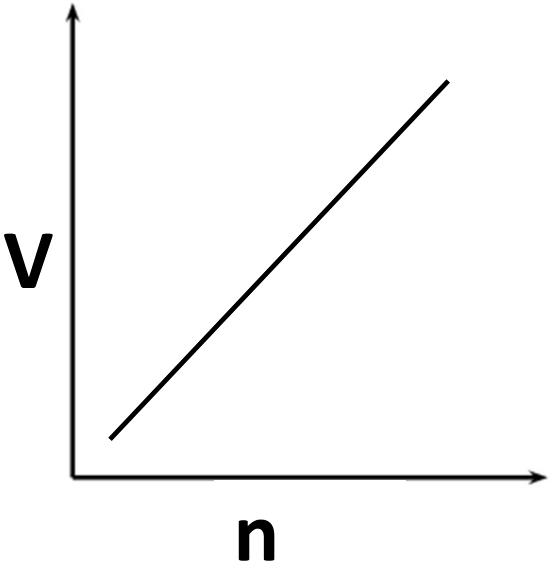
77 K

$$(1.30)\,(77.0)\,/\,(24.7 + 273.15) = V_2 \quad \Longrightarrow \quad V_2 = 0.336\ \text{L}$$

Avogadro's Law

At constant temperature (T) and pressure (P)

V and n are directly proportional



Which means:

$$\frac{V}{n} = \text{[a constant value]}$$

First state:
$V = V_1$ and $n = n_1$ ⇨ $\frac{V_1}{n_1}$ = [a constant]

Second state:
$V = V_2$ and $n = n_2$ ⇨ $\frac{V_2}{n_2}$ = [same constant]

⇨ $$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$ Avogadro's Law

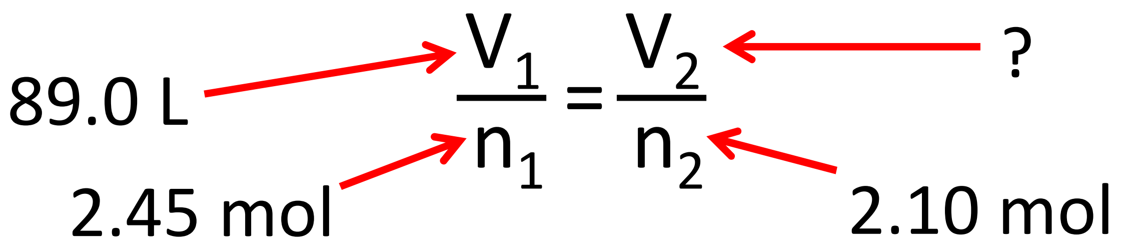
Example:

If 2.45 mol of argon gas occupies a volume of 89.0 L, what volume will 2.10 mol of argon* occupy under the same conditions of temperature and pressure?

We recognize this as an "Avogadro's Law" problem:

Pressure (P) and temperature (T) are constant

Number of moles (n) and volume (V) are changed



89.0 L

2.45 mol

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

?

2.10 mol

$$(89.0)\ (2.10)\ /\ (2.45) = V_2 \quad \Rightarrow \quad V_2 = 76.3 \text{ L}$$

* It wouldn't matter if the second state involved another gas, say, oxygen. What matters is the number of moles of whatever gas.

Combined gas law

We can combine Boyle's law and Charles' Law into a "combined" gas law:

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

Combined Gas Law

satisfies both laws when we hold constant the appropriate pairs of variables

Other "combined" gas laws can be derived

Boyle's Law & Avogadro's Law together give:

$$\frac{P_1 V_1}{n_1} = \frac{P_2 V_2}{n_2}$$

Charles' Law & Avogadro's Law together give:

$$\frac{T_1 n_1}{V_1} = \frac{T_2 n_2}{V_2}$$

These just demonstrate the idea of combining laws.
No need to memorize them.

We can combine Boyle’s Law, Charles’s Law, and Avogadro’s Law to obtain:

$$\frac{P_1\,V_1}{n_1\,T_1} = \frac{P_2\,V_2}{n_2\,T_2} \Rightarrow \frac{P\,V}{n\,T} = \text{constant}$$

Let’s call it the “Gas Constant”, and give it the symbol R

$$\Rightarrow \frac{P\,V}{n\,T} = R \Rightarrow \boxed{P\,V = n\,R\,T \quad \text{Ideal Gas Law}}$$

The units and value of R depends on the units of P, V, T, n

When the units are atm, L, K, mol, then

R = 0.08206 L atm/(mol K)

$PV = nRT$ Ideal Gas Law

It’s called the “Ideal Gas Law” because it corresponds to an “idealized” version of actual gases:

- Volume of the gas particles are negligible (zero)
- No attractive forces between gas particles

The second approximation means:

- The particles are unaware of one another’s existence
- Different gases mixed together are unaware of and undisturbed by one another

Other gas laws can be easily derived from PV=nRT

Red symbols can vary
Blue symbols are constant

$PV = nRT$ n , T constant

$PV = \text{constant}$ $P_1V_1 = P_2V_2$ Boyle's Law

$\frac{V}{T} = \frac{nR}{P}$ n , P constant

$\frac{V}{T} = \text{constant}$ $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ Charles' Law

$\frac{PV}{R} = nT$ P, V constant

$nT = \text{constant}$ $n_1T_1 = n_2T_2$ Un-named

Gay-Lussac’s Law

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

Can you derive it from the Ideal Gas Law?

How about a law relating P and n?

Recap: Gas laws and variables that are held constant

There are only 4 variables to consider.

- and one equation (Ideal Gas Law) tying them together.

If we hold **3** variables constant

The 4th one is determined from the other three.

- One equation, one unknown. You can solve for it.

If we hold **2** variables constant

The other 2 vary according to a “named law”

- Boyle’s Law, Charles’s Law, etc.
- they are either directly or inversely proportional

If we hold **1** variable constant

We get a “combined” gas law that ties together the other 3 variables

Deciding which law to use

1 variable constant, 3 variables changing

- If **P, V, T** are all changing, but **n** is constant (a common case), use the usual "**combined gas law**".
- You can also derive other "combined" gas laws if what's held constant is not **n**.

Deciding which law to use

2 variables constant, 2 variables changing

- Use “Named" laws like **Boyle's Law, Charles Law, etc.**
- Sometimes you need to derive an unnamed law from the ideal gas law

Deciding which law to use

3 variables constant

- The remaining 4th variable is found from the ideal gas law **PV = nRT**
- "3 variables constant" means the 4th one is also constant, but we just need to determine its value
- There is **no change** in any of the 4 variables
    - At least the relevant part of the problem won't involve a change in the state of the gas

Example:

An automobile tire at 23˚C with an internal volume of 25.0 L is filled with air to a total pressure of 3.18 atm. Determine the number of moles of air in the tire.

- We are given T, V, P
- No changes in them (three variables constant)

⇨ Use PV=nRT ⇨ $n = \frac{PV}{RT}$

Make sure we use Kelvins for T: $T_1 = 23 + 273.15 = 29\underline{6}.15\ \text{K}$

$$n = \frac{\overset{P}{(3.18\ \text{atm})}\overset{V}{(25.0\ \text{L})}}{\underset{R}{(0.08206\ \text{L atm mol}^{-1}\ \text{K}^{-1})}\underset{T}{(29\underline{6}.15\ \text{K})}} = 3.27\ \text{mol}$$

Example:

What is the pressure in a 304.0 L tank that contains 5.670 kg of helium at 25˚C?

- We are given V, mass (which can give n), T
- No changes in them (Three variables constant)

⇨ Use PV=nRT ⇨ $P = \frac{nRT}{V}$

Make sure we use Kelvins for T: $T_1 = 25 + 273.15 = 29\underline{8}.15\ \text{K}$

$$n = 5.670\ \text{kg}\ \frac{10^3\ \text{g}}{1\ \text{kg}}\ \frac{1\ \text{mol}}{4.0026\ \text{g}} = 141\underline{6}.4\ \text{mol}$$

$$P = \frac{\overset{n}{(1416.4\ \text{mol})}\overset{R}{(0.08206\ \text{L atm mol}^{-1}\ \text{K}^{-1})}\overset{T}{(29\underline{8}.15\ \text{K})}}{\underset{V}{(304.0\ \text{L})}} = 114\ \text{atm}$$

Example:

We have 121 mL of CO_2 gas at 27˚C and 1.05 atm. At what temperature **(in ˚C)** does it occupy a volume of 293 mL at a pressure of 1.40 atm?

- We are given V, T, P
- And another set of V, T, P
- Second T not known
- Three variables (V, T, P) change
- One variable (n) constant

⇨ Use the "combined gas law"

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

Make sure we use Kelvins for T: $T_1 = 27 + 273.15 = 30\underline{0}.15\text{ K}$

We can keep mL for V as long as we use the same units for V_1 and V_2

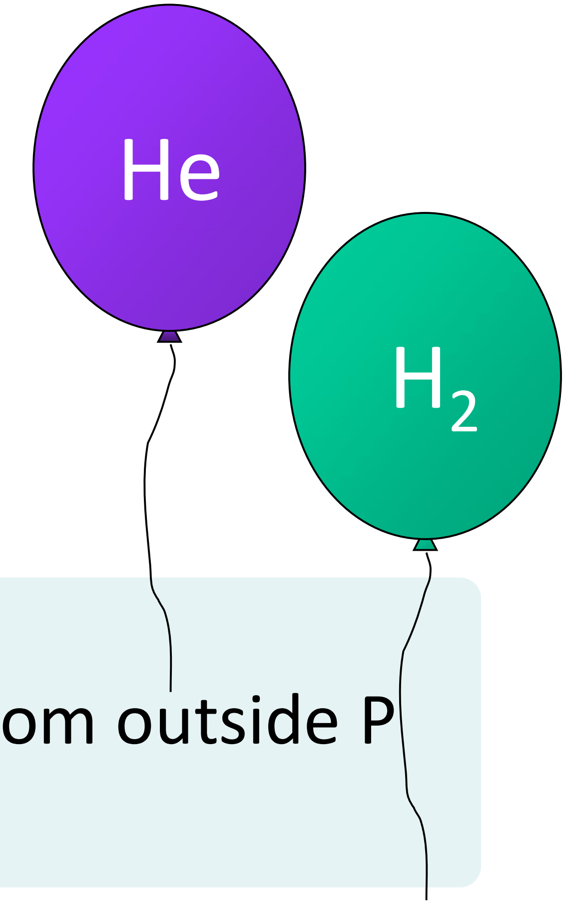
$$\frac{(1.05)(121)}{(30\underline{0}.15)} = \frac{(1.40)(293)}{T_2} \Longrightarrow T_2 = 969\text{K} = (969-273)\ ˚\text{C}$$

$$= \mathbf{696\ ˚C}$$

Work in Kelvins, then convert to ˚C if required

Concept Practice:

You are holding two balloons of the **same volume**. One contains helium, and one contains hydrogen. Answer the upcoming questions as “**different**” or “**the same**” and explain.



A balloon is not a rigid container

It cannot maintain a pressure different from outside P

$$P_{\text{balloon 1}} = P_{\text{room}} = P_{\text{balloon 2}}$$

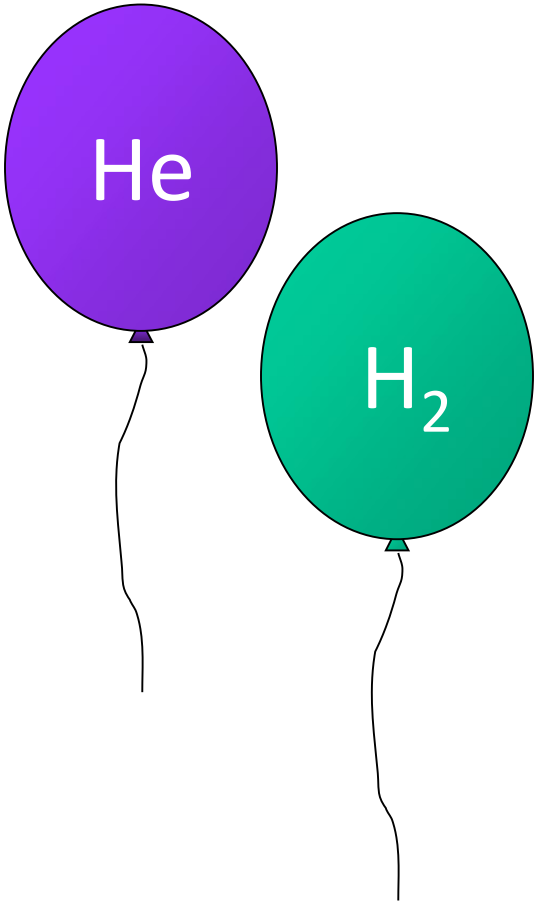
A balloon is not an insulating container

It cannot maintain a temperature different from outside T

$$T_{\text{balloon 1}} = T_{\text{room}} = T_{\text{balloon 2}}$$

Concept Practice:

The pressures of the gas in the two balloons are _the same____.



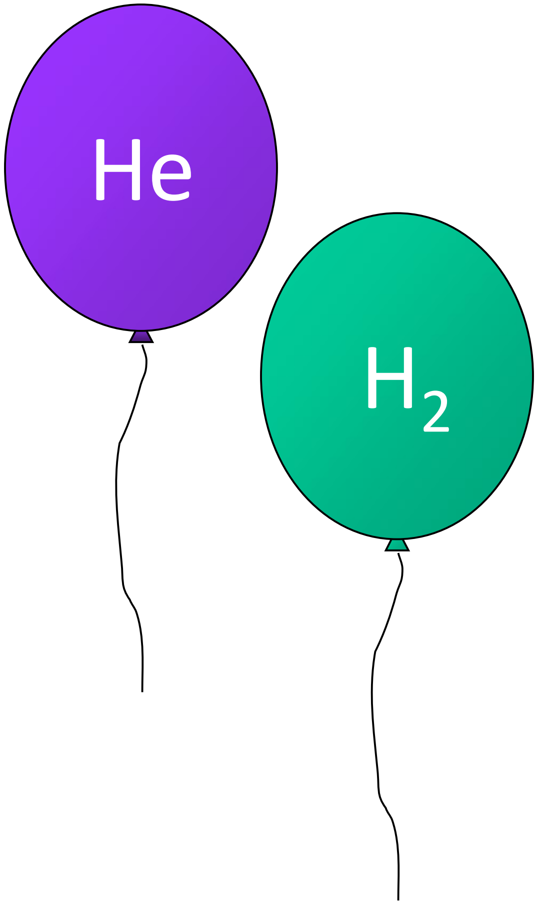
A balloon is not a rigid container

It cannot maintain a pressure that is different from outside pressure

$$P_{\text{balloon 1}} = P_{\text{room}} = P_{\text{balloon 2}}$$

Concept Practice:

The temperatures of the gas in the two balloons are __the same____.



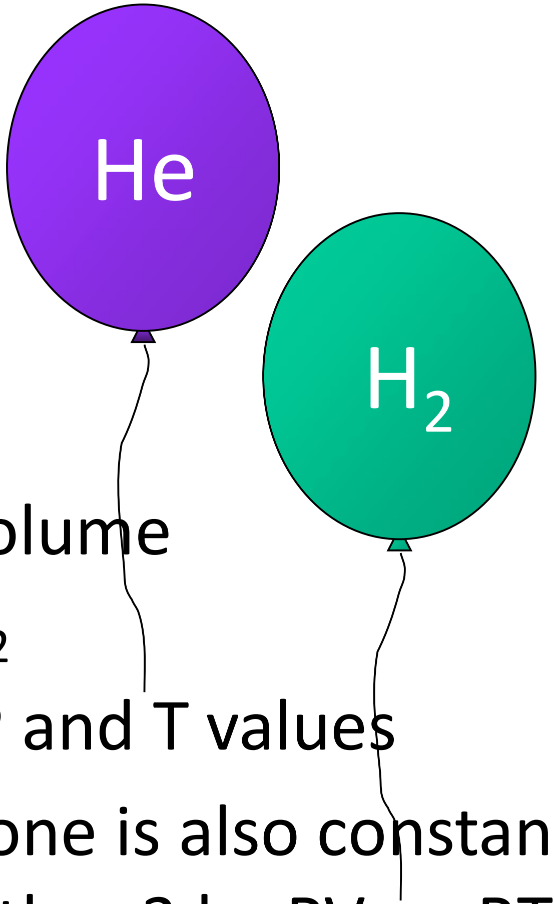
A balloon is not an insulating container

It cannot maintain a temperature that is different from outside temperature

$$T_{\text{balloon 1}} = T_{\text{room}} = T_{\text{balloon 2}}$$

Concept Practice:

The numbers of moles of the gas in the two balloons are the same.



- The question said they had the same volume

$$V_{\text{balloon 1}} = V_{\text{balloon 2}}$$

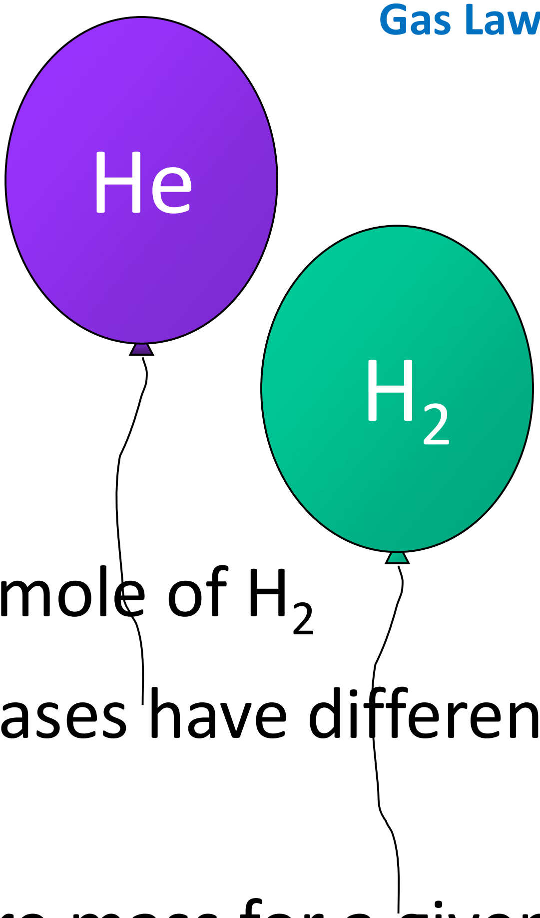
- We deduced that they have the same P and T values
- If 3 of the 4 variables are fixed, the 4th one is also constant.
  - Because it is determined from the other 3 by $PV = nRT$

$$n = \frac{\enclose{circle}{P}\enclose{circle}{V}}{R\enclose{circle}{T}}$$

A given set of P, V, T values dictates a unique value for n

Concept Practice:

The densities of the gas in the two balloons are **different**__________.



- A mole of He has a different mass than a mole of H_2
- Same number of moles of two different gases have different masses
- The one with greater molar mass has more mass for a given number of moles ($\boldsymbol{n}_{He} = \boldsymbol{n}_{H2}$) mass = (moles) × (molar mass)

  Since m.m.(He) = 4.00 g/mol; m.m. (H_2) = 2.02 g/mol
- Helium has almost double the mass of H_2 for a given $\boldsymbol{n}$
- Remember: density = **mass**/volume

Molar Volume of an Ideal Gas

By convention, a “standard temperature and pressure” (**STP**) has been defined as:

0˚C and **1 atm**

At **STP**, 1 mole of an ideal gas has a volume of **22.42 L**

- It is a convenient fact to memorize
- But we can readily find it by using the ideal gas law:

$$V = \frac{nRT}{P} = \frac{(1.000\ \cancel{\text{mol}})(0.08206\ \text{L}\cdot\cancel{\text{atm}}/\cancel{\text{K}}\cdot\cancel{\text{mol}})(273.2\ \cancel{\text{K}})}{1.000\ \cancel{\text{atm}}} = 22.42\ \text{L}$$

Molar Volume of an Ideal Gas

- Knowing that 1 mole of gas has 22.42 L of volume at 273.15 K and 1 atm gives us the same information as knowing the gas constant ***R.***
- In fact, to measure ***R*** experimentally, one would measure the **V** for a given **n**, **P**, **T**.
- STP is just one set of **n**, **P**, **T**, **V** values, always constrained only by the value of ***R***.

$$PV = nRT$$

$$R = \frac{PV}{nT} = \frac{(1\ \text{atm})\ (22.42\ \text{L})}{(1\ \text{mol})(273.15\ \text{K})} = 0.08208\ \frac{\text{atm L}}{\text{mol K}}$$

Last sig. fig. (uncertain) a bit different from the standard value (it’s normal)

Example:

A sample of oxygen gas has a volume of 2.50 L at STP. How many **grams** of O_2 are present?

Before we find the mass, we need to find the moles

We can use the ideal gas law $PV=nRT$

$$n = \frac{PV}{RT} = \frac{(1\text{ atm})\,(2.50\text{ L})}{(0.08206)(273.15\text{ K})} = 0.11\underline{1}5\text{ mol}$$

But it's a lot simpler to use the molar volume at STP:

$$2.50\text{ L} \times \frac{1\text{ mol}}{22.42\text{ L}} = 0.11\underline{1}5\text{ mol}$$

$$0.11\underline{1}5\text{ mol} \times \frac{32.00\text{ g}}{1\text{ mol}} = \boxed{3.57\text{ g}}$$

m.m. O_2 = 32.00 g/mol

Example:

What is the density of F_2 at STP (in g/L)?

At STP, for 1 mol of gas, **V=22.42 L**

Since density is mass/volume, we convert mol to mass:

m.m. F_2 = 38.00 g/mol

$$\textbf{mass} = 1\text{ mol} \times \frac{38.00\text{ g}}{1\text{ mol}} = \mathbf{38.00\ g}$$

$$d = \frac{\text{mass}}{V} = \frac{38.00\text{ g}}{22.42\text{ L}} = 1.695\text{ g/L}$$

Calculating the **molar mass** (*M*) of a gas from **density**

$$PV = nRT \qquad M = \frac{\overset{\text{mass}}{m}}{n} \rightarrow n = \frac{m}{M}$$

$$\downarrow$$

$$PV = \frac{m}{M}RT$$

$$\downarrow$$

$$M = \frac{m}{V}\,\frac{RT}{P} \rightarrow \boxed{M = d\,\frac{RT}{P}}$$

It's good to know how
it's derived,
but it's convenient to
know and use it
directly instead of
deriving it every time.

$$M = d\,\frac{RT}{P}$$

tells us that gases with higher density have higher molar masses

We can rearrange it to calculate density (d) from molar mass (M):

$$\boldsymbol{d = M\,\frac{P}{RT}}$$

which tells us that higher molar mass leads to higher density for gases.

Example:

When 0.960 g of a liquid is vaporized at 110.°C and 0.967 atm, the gas occupies a volume of 0.559 L. What is the molar mass of the compound?

We can calculate molar mass of a gas if we know its density at a given P, V, T: $M = d\,\frac{R\,T}{P}$

All of the liquid (0.960 g) became gas, occupying 0.559 L

$\boldsymbol{d}$ = (0.960 g)/(0.559 L) = 1.7$\underline{1}$7 g/L

$$M = d\,\frac{R\,T}{P} = (1.7\underline{1}7)\,\frac{(0.08206)(110.+273)}{(0.967)} = 55.8\text{ g/mol}$$

Check the units to make sure they cancel and give g/mol

Same Example; alternative (and better) solution:

When 0.960 g of a liquid is vaporized at 110.°C and 0.967 atm, the gas occupies a volume of 0.559 L. What is the molar mass of the compound?

Given T, P, V, we can calculate n from PV=nRT:

$$n = \frac{PV}{RT} = \frac{(0.967)(0.559)}{(0.08206)(110.+273)} = 0.0172 \text{ mol}$$

Mass, m, of the gas (same as in liquid form) is 0.960 g

Molar mass can be calculated from "mass per moles" of a given sample:

$$M = \frac{m}{n} = \frac{0.960 \text{ g}}{0.0172 \text{ mol}} = 55.8 \text{ g/mol}$$

Here we bypassed density in calculating the molar mass

Partial Pressures

Partial Pressure of an ideal gas:

- **The pressure it would exert if it were alone**

For a mixture of ideal gases in a container,

$$P_{Total} = P_1 + P_2 + P_3 + \ldots$$

The total pressure exerted is the <u>sum of the pressures</u> that each gas would exert if it were <u>alone</u>.

- Remember that ideal gas particles don’t interact, so they are “unaware” of other gases in the same container
- So the presence of another gas has no effect on what pressure a gas would generate by itself. The pressures simply add up.

Partial Pressures

Gas 1 alone

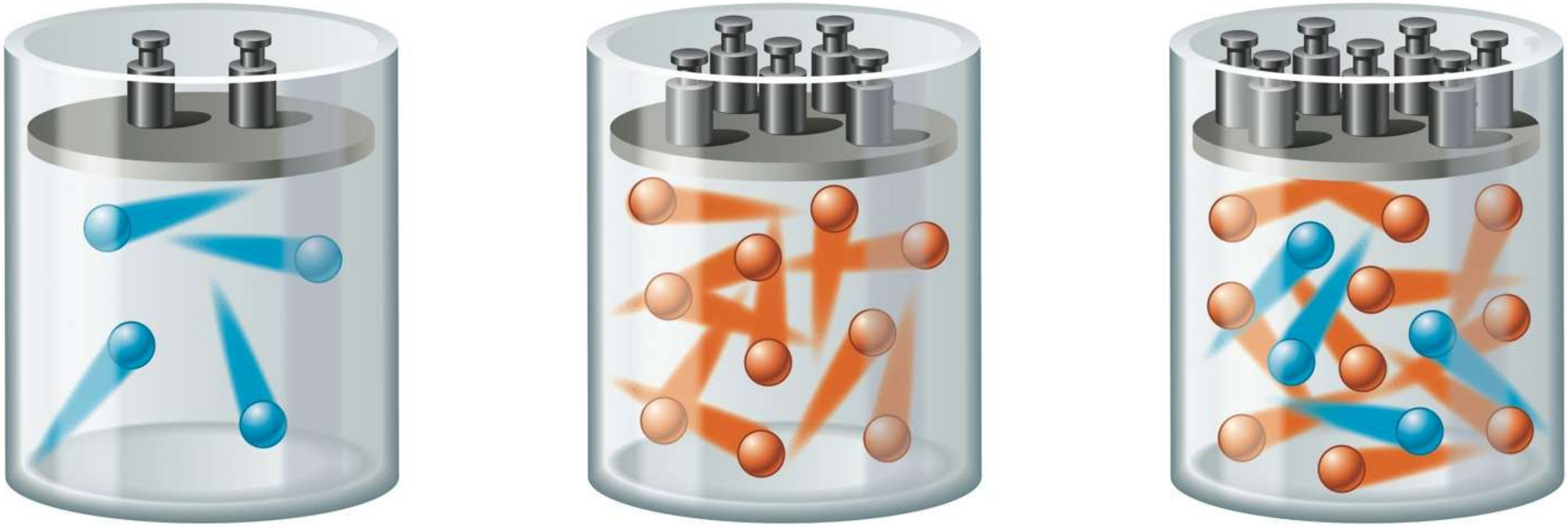
P_1

Gas 2 alone

P_2

Gas 1 + Gas 2

$P = P_1 + P_2$



Example:

27.4 L of oxygen gas at 25.0˚C and 1.30 atm, and 8.50 L of helium gas at 25.0˚C and 2.00 atm were pumped into a tank with a volume of 5.81 L at 25˚C. Calculate the partial pressures of oxygen and helium in the tank, as well as the total pressure.

Both gases go from their original container to the same new tank (new V). We will think about them separately.

Each gas preserves its number of moles, and temperature remains the same at 25.0˚C. This means constant **n** and **T**.

At constant **n** and **T**, we have **P** and **V** changing, following Boyle's Law:

$$\mathbf{P_1 V_1 = P_2 V_2}$$

For O_2: $(1.30)(27.4) = P_2(5.81)$ $P_2 = 6.13$ atm $= \mathbf{P_{O_2}}$

For He: $(2.00)(8.50) = P_2(5.81)$ $P_2 = 2.93$ atm $= \mathbf{P_{He}}$

$\mathbf{P_{total}} = P_{O_2} + P_{He} = 6.13 + 2.93 = 9.06$ atm

Mole Fractions

mole fraction of A: $\boxed{x_A = \frac{n_A}{n_{total}}}$

Mole fraction is particularly useful with <u>partial pressures</u>

$P_A = x_A\, P_{total}$ $\boxed{x_A = \frac{P_A}{P_{total}}}$

Mole fractions are like "pressure fractions"

$$x_A + x_B + x_C + \cdots = 1$$

$$P_A + P_B + P_C + \cdots = P_{total}$$

Example

The partial pressures of CH_4, N_2, and O_2 in a sample of gas were found to be 135 mmHg, 508 mmHg, and 571 mmHg, respectively. Calculate the mole fraction of nitrogen.

Mole fractions are also like "pressure fractions"

$$x_{N_2} = \frac{P_{N_2}}{P_{total}}$$

$$P_{total} = P_{CH_4} + P_{N_2} + P_{O_2} = 135+508+571 = 1214 \text{ mmHg}$$

$$x_{N_2} = \frac{508 \text{ mmHg}}{1214 \text{ mmHg}} = 0.418$$

Kinetic Molecular Theory

So far we have considered "**what** happens" (Gas **Laws**) but not the "why" or the "how" of it.

Natural laws tell us what should happen, but don't explain the "mechanics" behind that.

A theory explains **why** the law exists.

Kinetic Molecular Theory explains the ideal gas laws.

Postulates of the Kinetic Molecular Theory

Basic assumptions

1. The particles are so small compared with the distances between them that the volume of the particles can be assumed to be negligible.

In other words:

Particles have no volume

Entire gas volume is the empty space between particles

No volume contributed by particles themselves

Postulates of the Kinetic Molecular Theory

2. The particles are in constant motion and their **collisions with the container walls are the origin of the pressure** exerted by the gas.

Not so much an "assumption".

More of an observation that the collisions are the only source to apply a force on the container walls.

Postulates of the Kinetic Molecular Theory

3. **The particles exert no forces on each other**

Importantly:

Particles don’t attract each other

What about repelling each other? Well, not that either, but in any case intermolecular forces are always attractive except during collisions

They can bounce off each other elastically, but mathematically it’s the same as passing through each other

Postulates of the Kinetic Molecular Theory

4. The **average kinetic energy** of the gas particles is **directly proportional to the Kelvin temperature** of the gas.

Basically the <u>definition</u> of Kelvin temperature scale, rather than an "assumption".

What makes an ideal gas “ideal”?

Two of the postulates. Rephrased, we have:

“Particles have no volume”

“No intermolecular forces”

Root Mean Square Velocity

A kind of **average velocity** useful in kinetic molecular theory

“Square root of the average of the squares of the particle velocities”

$$u_{rms} = \sqrt{\frac{3RT}{M}}$$

R = 8.3145 J/K·mol
(gas constant **expressed in SI units)**
J = joule = kg·m^2/s^2 (SI energy unit)

T = temperature of gas (in K)

M = molar mass **in kilograms** (kg/mol)
(kg is the SI unit for mass)

Resultant units are in **m/s**

Why "Root Mean Square Velocity"? — instead of ordinary average?

We just show here u_{rms} (and not the ordinary average of velocity) is the important one. No need to memorize anything here, or worry if you don't fully follow.

$T \propto$ (average kinetic energy)

u = velocity of particles

(average kinetic energy) = $\frac{1}{2}m(u^2)_{av}$

average of the square (of u) is related to the temperature, not the "regular" average of u (they are somewhat different)

$$T \propto (u^2)_{av}$$

$$u_{rms} = \sqrt{(u^2)_{av}}$$

$$T \propto (u_{rms})^2$$

$$\sqrt{T} \propto u_{rms}$$

$$u_{rms} \propto \sqrt{T}$$

The full relationship turns out to be:

$$\boxed{u_{rms} = \sqrt{\frac{3RT}{M}}}$$

Quick reminder on algebra

$$\sqrt{\frac{3RT}{M}} = \frac{\sqrt{3}\sqrt{R}\sqrt{T}}{\sqrt{M}} = \sqrt{3R}\,\frac{\sqrt{T}}{\sqrt{M}} = \sqrt{3R}\;\sqrt{T}\;\frac{1}{\sqrt{M}}$$

Root Mean Square Velocity

$$u_{rms} = \sqrt{\frac{3RT}{M}}$$

So, u_{rms} is:

- directly proportional to $\sqrt{T}$
- **inversely** proportional to $\sqrt{M}$

The rates of two important physical processes

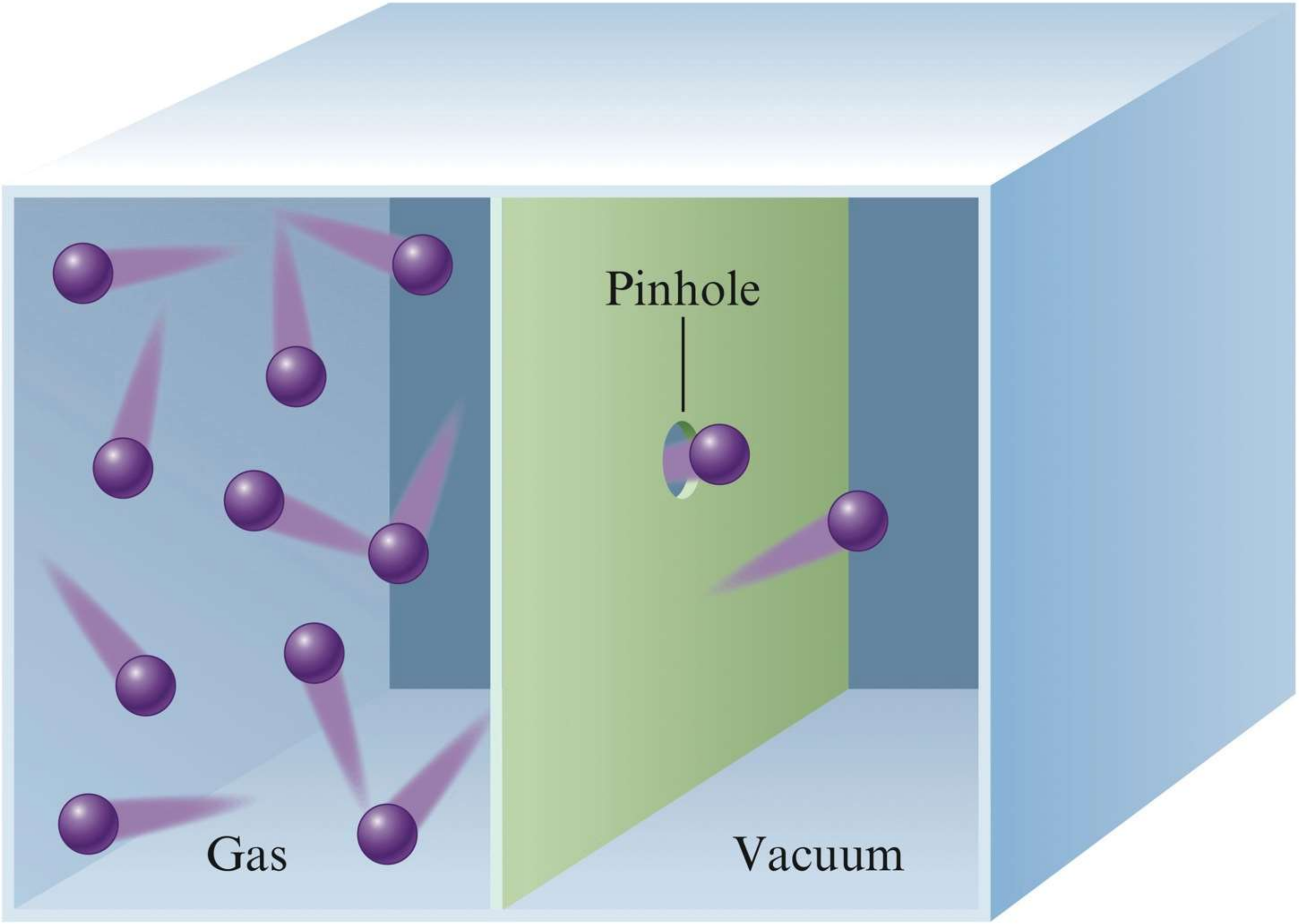
- Effusion
- Diffusion

are also directly proportional to $\mathbf{u_{rms}}$.

So those rates are also

- directly proportional to $\sqrt{T}$
- inversely proportional to $\sqrt{M}$

Effusion: passage of a gas through a tiny orifice into an empty chamber (vacuum).

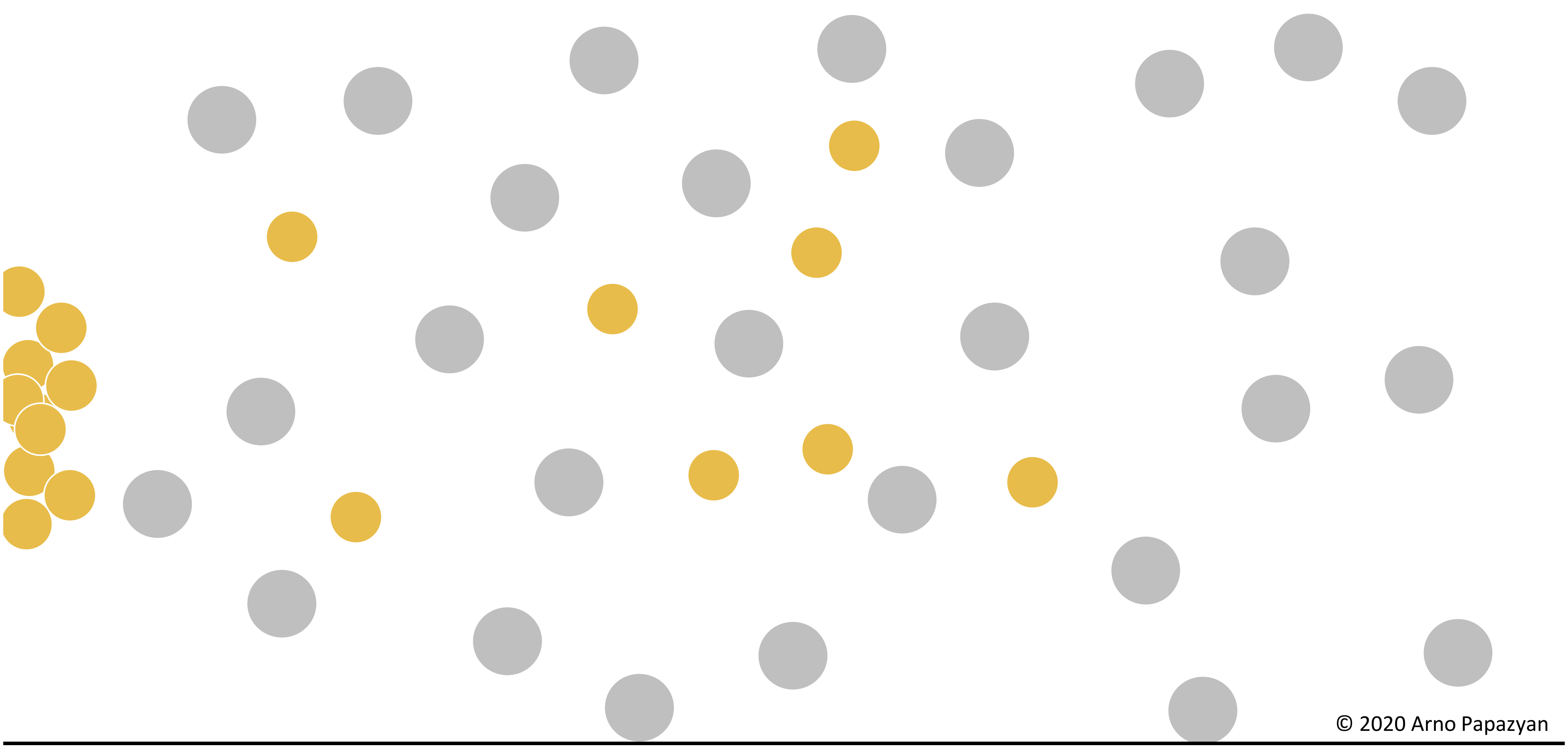


Rate of effusion measures the speed at which the gas is transferred into the chamber.

Diffusion: one gas spreading through another gas

🟡 Particles that are doing the diffusing

● Particles through which 🟡 diffuse
(shown stationary in the animation below;
they actually move, like all particles do)



Graham's Law

- Applies to both **effusion** & **diffusion** rates
- Exact for ideal gases
- Approximate for non-ideal gases

Since rate is directly proportional to $u_{rms} = \sqrt{\dfrac{3RT}{M}}$

Rate is directly proportional to $\dfrac{1}{\sqrt{M}}$

Rate is **inversely** proportional to $\sqrt{M}$

$$\frac{(u_{rms})_{Gas\,1}}{(u_{rms})_{Gas\,2}} = \boxed{\frac{\text{Rate for Gas }\enclose{circle}{1}}{\text{Rate for Gas }\boxed{2}} = \frac{\sqrt{M_{\boxed{2}}}}{\sqrt{M_{\enclose{circle}{1}}}}}$$

Caution!

Rate is **<u>inversely</u> proportional** to **time**

When comparing the **<u>time</u>** it takes for gases to diffuse a certain distance or a certain amount of gas to effuse through a pinhole:

$$\textbf{Time} \propto \sqrt{\mathbf{M}}$$

! ! !

$$\boxed{\frac{\textbf{Time}\text{ for gas }\textcircled{1}}{\textbf{Time}\text{ for gas }\boxed{2}} = \frac{\sqrt{M_{\textcircled{1}}}}{\sqrt{M_{\boxed{2}}}}}$$

Note how it's different from the ratio of rates

For examples and practice questions involving effusion and diffusion problems, please use the “Practice Questions” and “Suggested end-of-chapter Questions” posted under the resource page of this chapter at papazyan.org

Real Gases (as opposed to “ideal” gases)

- An ideal gas is a very useful but a theoretical concept. No gas exactly follows the ideal gas law.
- Gases deviate from ideal gas law when
  - ➢ the molar density **n/V** is <u>high</u>

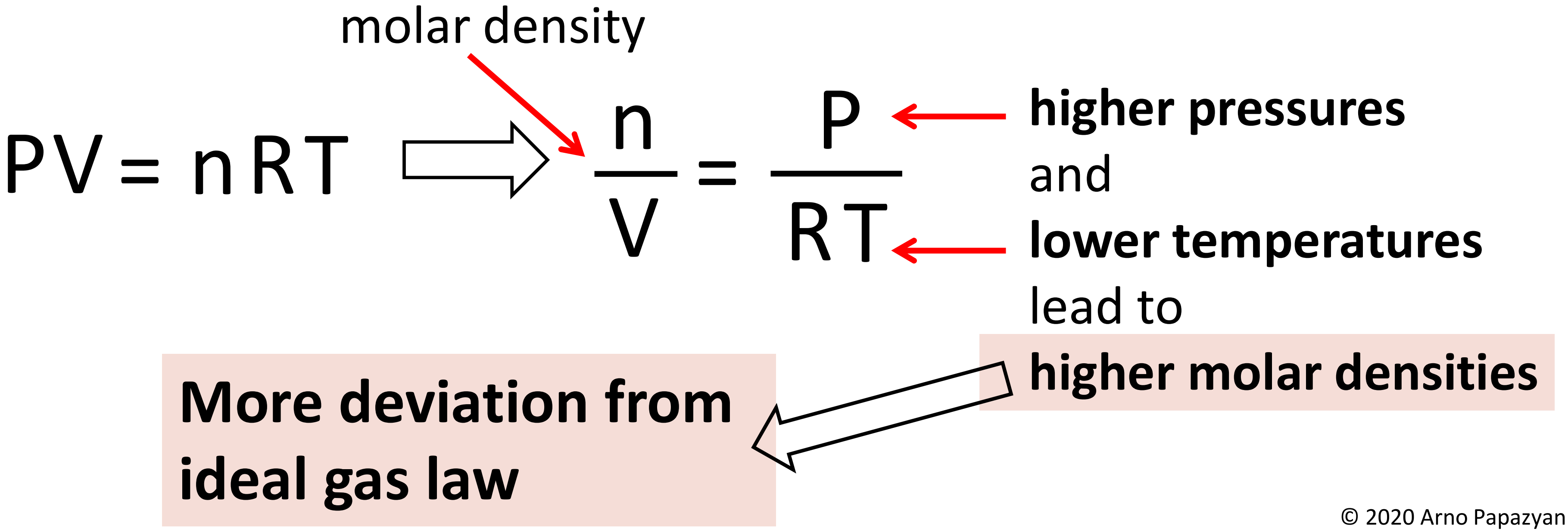
    i.e. “too many” particles in a given volume

When the molar density is high, the average distance between particles is small enough, so that:

- Attractive forces become significant
- Volume of gas particles (assumed zero for ideal gas) **become a significant fraction** of gas volume

Higher pressures and lower temperatures lead to deviation from the ideal gas law

Even though we are talking about deviating from the ideal gas law, we can still use its guidance about when we get high density. After all, to get to high density, we start from low density (where ideal gas law applies), and PV=nRT can tell us which direction takes us to higher density.



molar density

$$PV = nRT \Rightarrow \frac{n}{V} = \frac{P}{RT}$$

higher pressures
and
lower temperatures
lead to
higher molar densities

More deviation from ideal gas law

Effect of particle volume on the volume of real gases

The volume of a gas is the volume of the particles plus the volume between particles.

$$V = V_{\text{particles}} + V_{\substack{\text{between}\\\text{particles}}}$$

But for an “ideal gas”, $V_{\text{particles}} = 0$

$$\Rightarrow V = V_{\substack{\text{between}\\\text{particles}}} \qquad \Rightarrow V_{\text{ideal}} = V_{\substack{\text{between}\\\text{particles}}}$$

The volume V in the ideal gas law actually corresponds to the <u>volume between particles</u>.

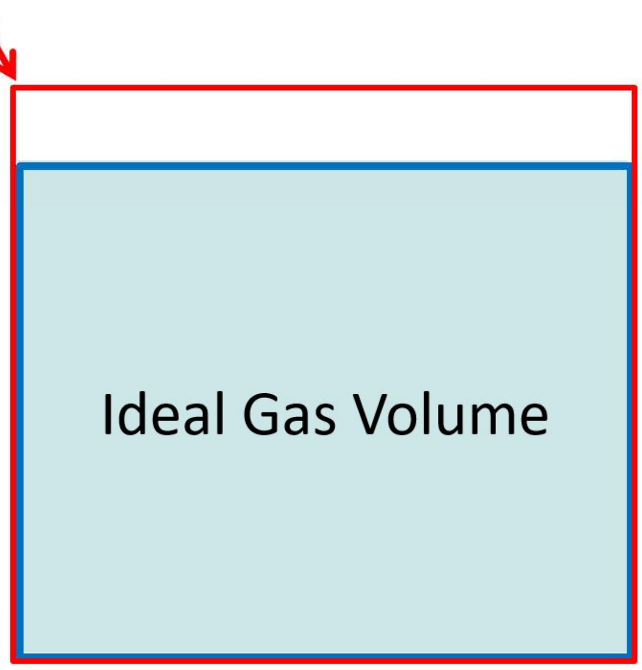
$$P\,V_{\substack{\text{between}\\\text{particles}}} = n\,R\,T$$

Effect of particle volume on the volume of real gases

But real gas particles have some volume: $V_{particles} > 0$

$$V_{real} = V_{ideal} + V_{particles}$$

$$\boxed{V_{real} > V_{ideal}}$$



● Particles

▨ Volume between particles

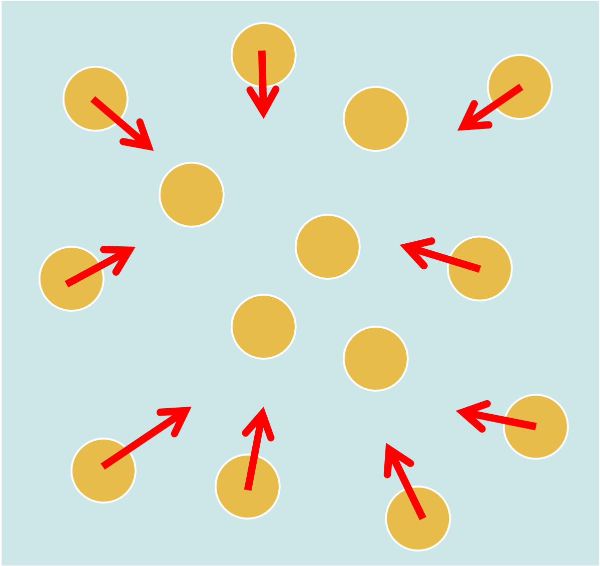
Effect of particle volume on the volume of real gases

Note that we can use a modified ideal gas law if we subtract the volume of particles from the real gas volume

$$P\,\underbrace{(\overset{V_{\text{real}}}{V}-V_{\text{particles}})}_{V_{\text{ideal}}} = n\,R\,T$$

Effect of **inter-particle attractions** on real gases

In a real gas, **attractions between particles** pull them away from container walls



We know qualitatively: Inter-particle attractive forces **decrease real gas pressure** compared with ideal gas

$$P_{real} < P_{ideal}$$

For a **real gas**:

- The actual **observed volume is larger** than the volume expected for an ideal gas due to the volume of the gas particles themselves, which is a “dead” volume into which other gas particles cannot travel.

- The actual **observed pressure is lower** than the pressure expected for an ideal gas due to the intermolecular attractions that occur in real gases.