CEM 152

Web page;
https://www2.chemistry.msu.edu/courses/cem152/



Chapter 10

Gases

10.1 Physical Characteristics of Gases

- **Physical properties of gases are all similar.**
- **Composition**
  - nonmetallic elements
  - low molar masses.
- **Unlike liquids and solids, gases:**
  - expand to fill their containers.
  - are highly compressible.
  - have extremely low densities.
- **Two or more gases form a homogeneous mixture.**

Some Common Gases

Table 10.1 Some Common Compounds That Are Gases at Room Temperature

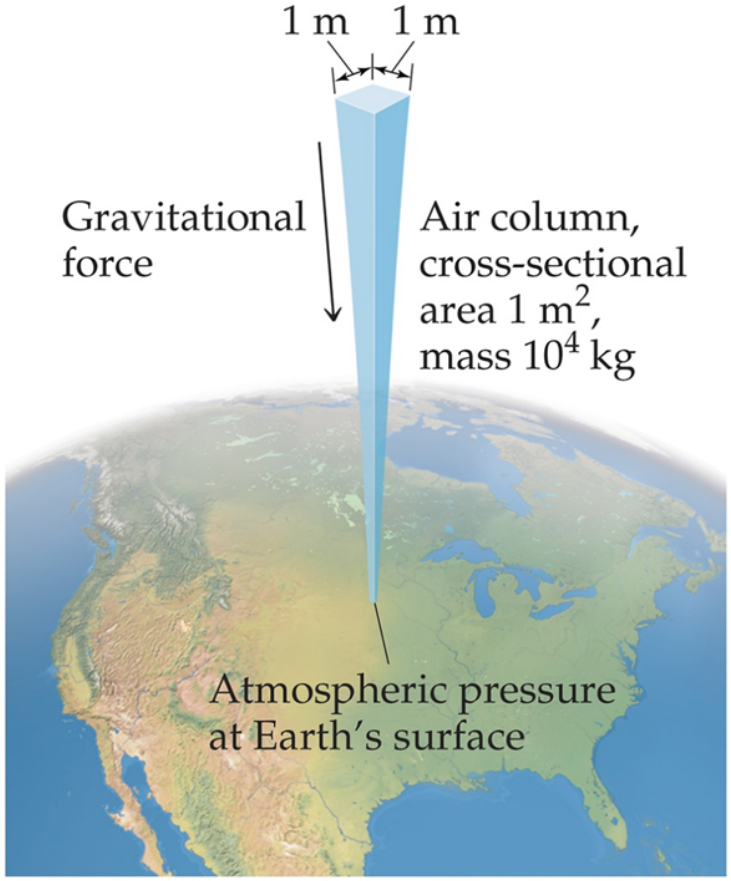
Formula	Name	Characteristics
HCN	Hydrogen cyanide	Very toxic, slight odor of bitter almonds
H_2S	Hydrogen sulfide	Very toxic, odor of rotten eggs
CO	Carbon monoxide	Toxic, colorless, odorless
CO_2	Carbon dioxide	Colorless, odorless
CH_4	Methane	Colorless, odorless, flammable
C_2H_4	Ethene (Ethylene)	Colorless, ripens fruit
C_3H_8	Propane	Colorless, odorless, bottled gas
N_2O	Nitrous oxide	Colorless, sweet odor, laughing gas
NO_2	Nitrogen dioxide	Toxic, red-brown, irritating odor
NH_3	Ammonia	Colorless, pungent odor
SO_2	Sulfur dioxide	Colorless, irritating odor

Pressure

- **Pressure** is the amount of force applied to an area:

$$P = \frac{F}{A}$$

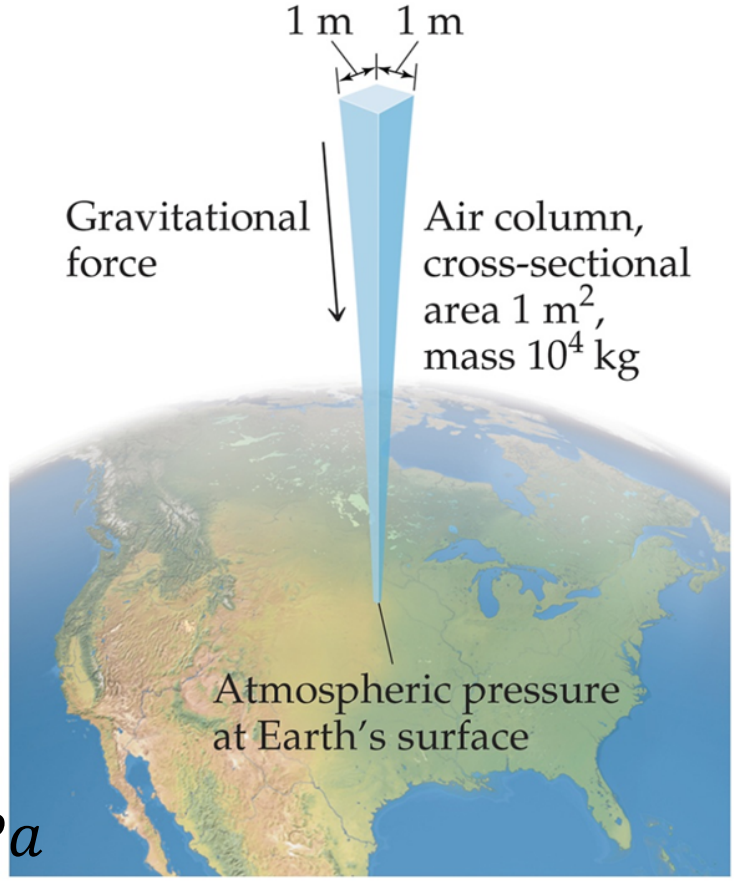
- Gases: **All** exert pressure on any surface they contact.
- **Atmospheric pressure** is the weight of air per unit of area.



Pressure

- **Pressure** is the amount of force applied to an area:

$$P = \frac{F}{A}$$

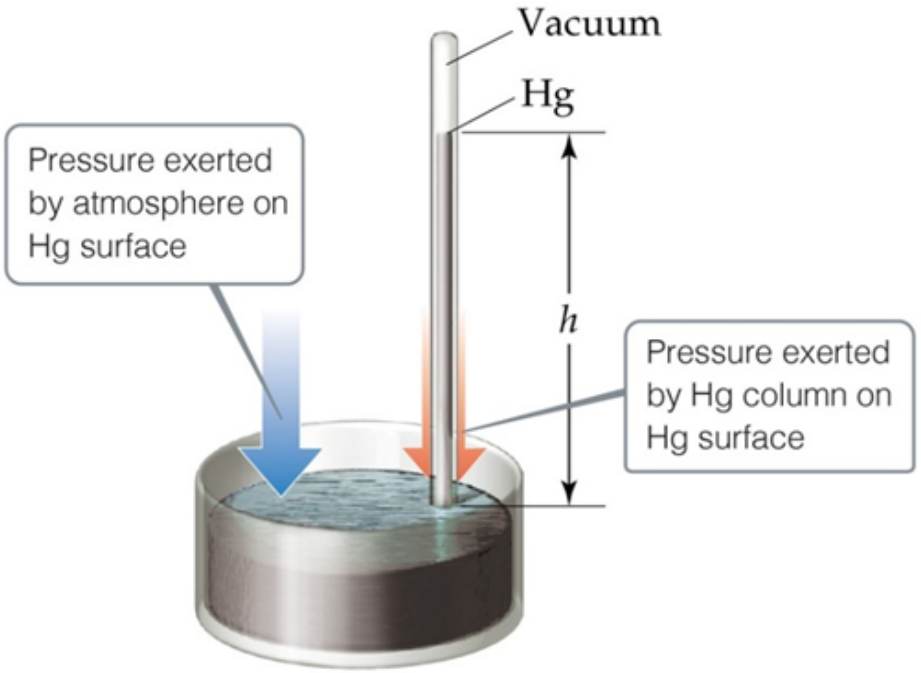


F = (10,000 kg)(9.8 m/s^2)
$\approx$ 100,000 kg $\cdot\, m/s^2$
$= 10^5\ N$

$$P = \frac{F}{A} = \frac{10^5\ N}{1\ m^2} = 10^5\ N/m^2 = 10^5\ Pa$$

Units of Pressure

- **Pascals:** $1\,\text{Pa} = 1\ \text{N/m}^2$ (SI unit of pressure)
- **Bar:** $1\,\text{bar} = 10^5$ Pa = 100 kPa
- **mm Hg or torr:**
  - Difference in height of Hg
    - Between vacuum
    - And gas pressure to be measured.

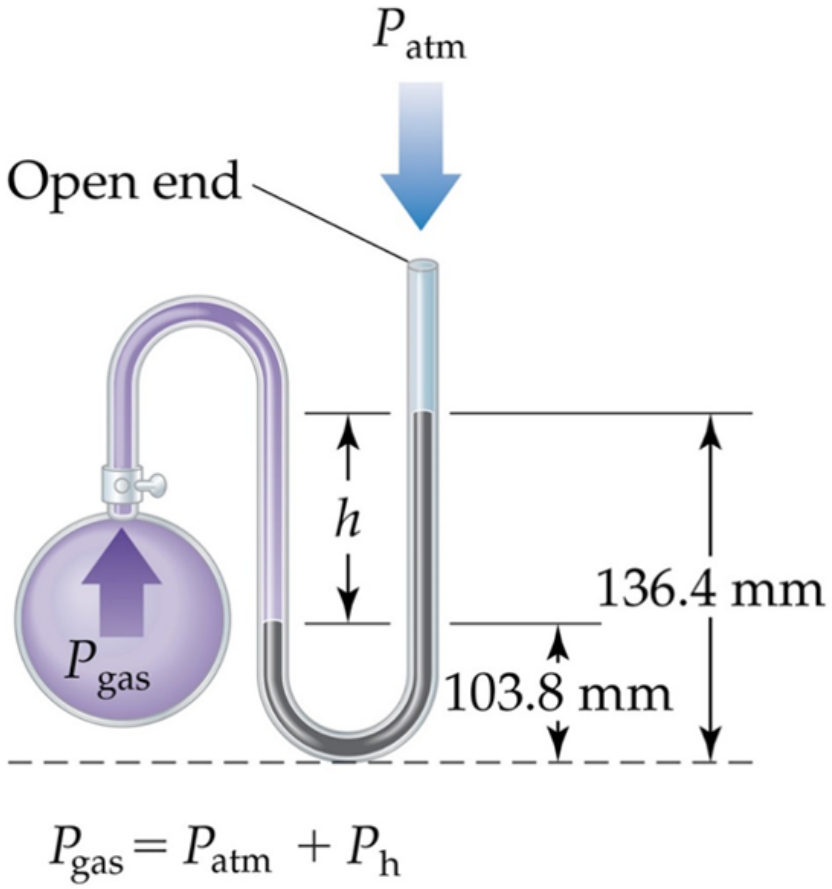


Standard Pressure

- Normal atmospheric pressure at sea level is referred to as ***standard atmospheric pressure***.
- 1 atm is equal to
  - 760 torr
  - 760 mm Hg
  - 101.325 kPa
  - 1.01325 bar

Manometer

- The **manometer** is used to measure the difference in pressure between *atmospheric* pressure and that of a gas in a vessel.
- For a gas at a higher pressure (P_{gas}) than atmospheric pressure (P_{atm}), $P_{gas} = P_{atm} + P_h$ where P_h is the difference in height of the mercury column.



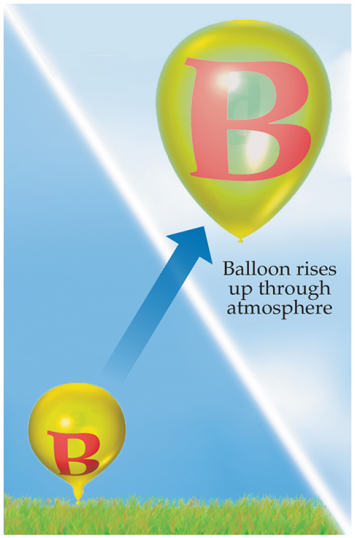
10.2 The Gas Laws

Four variables define the *state*, of a gas:

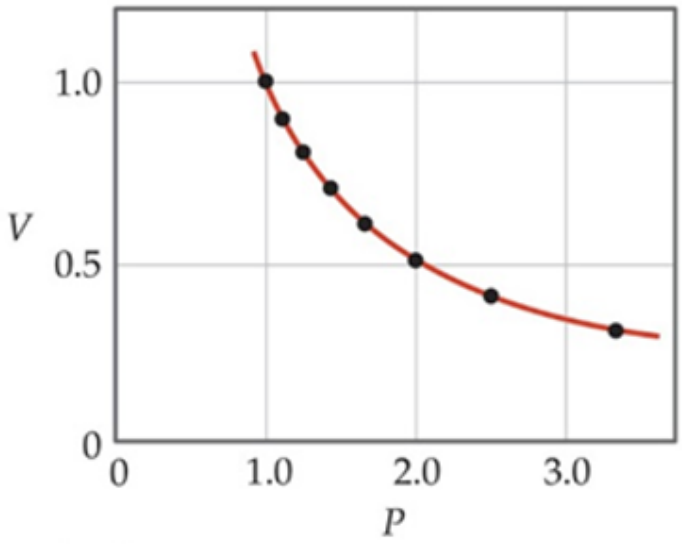
1) Temperature
2) Pressure
3) Volume
4) number of moles of gas

Pressure–Volume Relationship: Boyle's Law

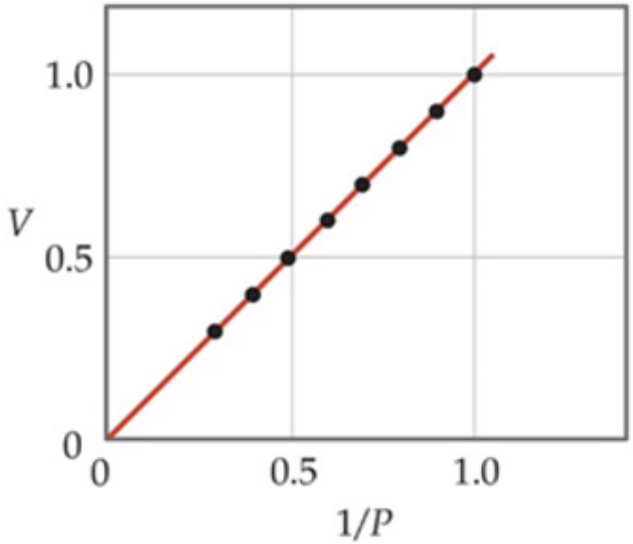
- The volume of a fixed quantity of gas at constant temperature is inversely proportional to the pressure.



- V = Constant/P
- *PV* = Constant. $P_1V_1=P_2V_2$
- V versus P not linear



V versus 1/P, linear.

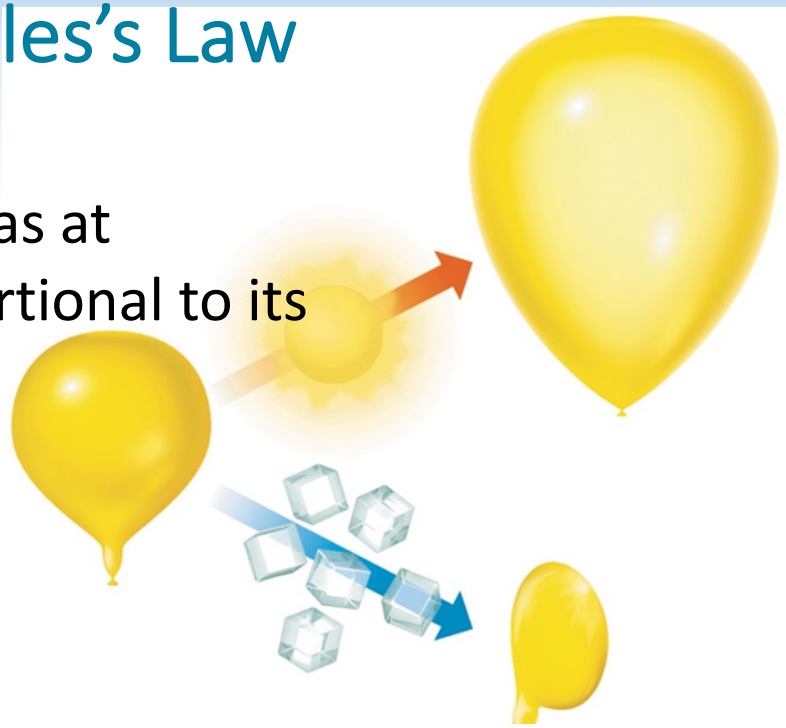


Temperature–Volume: Charles's Law

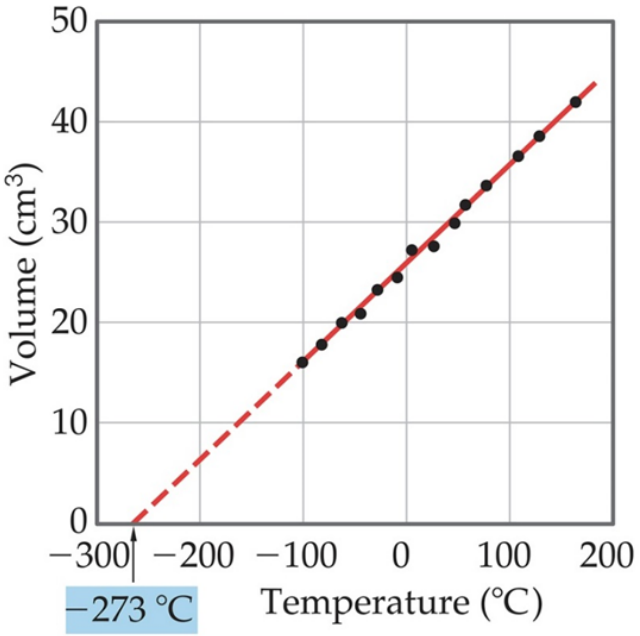
- The volume of a fixed amount of gas at constant pressure is directly proportional to its absolute temperature.

- $V = \text{Constant} \times T$.

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



A graph of *V* versus *T*, is linear.



Amount–Volume : Avogadro's Law

- The volume of a gas at constant temperature and pressure is directly proportional to the number of moles of the gas.
- So, at STP, one mole of **ANY** gas occupies 22.4 L.
- Mathematically:



Volume	22.4 L	22.4 L	22.4 L
Pressure	1 atm	1 atm	1 atm
Temperature	0 °C	0 °C	0 °C
Mass of gas	4.00 g	28.0 g	16.0 g
Number of gas molecules	6.02×10^{23}	6.02×10^{23}	6.02×10^{23}

$$V = \text{constant} \times n, \text{ or } \frac{V_1}{n_1} = \frac{V_2}{n_2}.$$

10.3 The Ideal-Gas Equation

- Combining:

$$V \propto \frac{1}{P} \text{ (Boyle's law).}$$

$$V \propto T \text{ (Charles's law).}$$

$$V \propto n \text{ (Avogadro's law).}$$

- we get:

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

- Finally, to make it an equality, we use a constant of proportionality (R) and reorganize; this gives the ideal-gas equation:
- ***P V = n R T.***

R—The Ideal Gas Constant

Table 10.2 Numerical Values of the Gas Constant *R* in Various Units

Unit	Numerical Value
L - atm/mol - K	0.08206
J / Mol K	8.314
cal / mol K	1.987
m^3 - Pa/mol - K *	8.314
L - torr / mol - K	62.36

- 0°C and 1 bar is referred to as standard temperature and pressure (**STP**).
- The volume of one mole of ideal gas at STP is 22.4 L.

Relating the Ideal Gas Equation and the Gas Laws

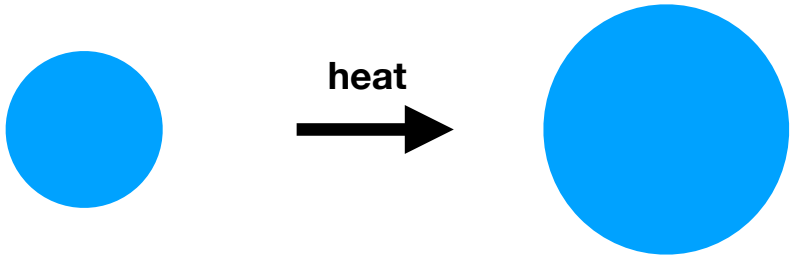
- $PV = nRT$ = constant
- $PV / T = nR = \text{constant}$ so $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$
- In solving problems:

1. Tabulate the information.
2. Convert to consistent units.
3. Pick or rearrange the Ideal gas law.
4. Use dimensional analysis.

Do as many problems as possible to become proficient.

Example Gas Law Question 1

A) 2 L of an ideal gas is **heated** from 50 °C to 150 °C **under a constant pressure** of 1 atm; what happens to the volume?



P_1V_1

$$P_1V_1 = nRT_1 \qquad P_1V_2 = nRT_2$$

$$\frac{P_1V_1}{RT_1} = n$$

$$\frac{(1atm)(2L)}{323K(.08206\ L\ atm\ mole^{-1}K^{-1}} = 0.07496mole$$

$$V_2 = \frac{nRT_2}{P_1}$$

$$\frac{0.07496mole(.08206L\ atm\ mole^{-1}K^{-1})423K}{1atm}$$

= 2.62 L

Gas Densities from Ideal Gas Law

The ideal gas law can also be written in terms of gas density (mass per volume) and molar mass:

Ideal gas law
With regard to mol

$$PV = nRT$$

$$PV = \left(\frac{m}{M}\right)RT$$

$$PM = \left(\frac{m}{V}\right)RT$$

***m*: total mass**
***M*: molar mass, m/mol**
***n*: number of moles**

n = m/M

***Density (d)** = m/V*

Ideal gas law
With regard to density

$$PM = dRT$$

Example:

What is the density of methane (CH_4) at 1 atm and 27 ^oC?

$$PM = dRT$$

Ideal gas law with regard to density

$$d = \frac{PM}{RT}$$

$$= \frac{1\ \text{atm} \times 16\ \text{g} \cdot \text{mol}^{-1}}{0.08206\ \text{atm} \cdot \text{L} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 300.15\ \text{K}}$$

Molar mass of CH_4

Absolute T

$$= 0.65\ \text{g} \cdot \text{L}^{-1}$$

Gas Laws and reaction stoichiometry

An example:

Automobile airbags are inflated by the rapid generation of N_2 gas produced by the decomposition of sodium azide:

$$2NaN_{3(s)} \longrightarrow Na_{(s)} + 3N_{2(g)}$$

If the inflated bag volume is 56 L and the pressure is 15% greater than the average atmospheric pressure at 20 ^{o}C, how many grams of sodium azide are required?

Gas Laws and reaction stoichiometry

$$2\mathrm{NaN}_{3(s)} \longrightarrow \mathrm{Na}_{(s)} + 3\mathrm{N}_{2(g)}$$

Step 1. Use the gas law to find the number of moles of N_2 necessary to produce the pressure:

Final pressure

Final volume

$$n_{\mathrm{N_2}} = \frac{PV}{RT} = \frac{1.15\ \mathrm{atm} \times 56\ \mathrm{L}}{0.08206\ \mathrm{atm \cdot L \cdot K^{-1} \cdot mol^{-1}} \times 293.15\ \mathrm{K}} = 2.68\ \mathrm{mol}$$

Step 2. Find out how many moles of NaN_3 are needed to produce this amount of N_2:

From the balanced equation, 2 moles of NaN_3 are consumed to produce 3 moles of N_2.

$$n_{\mathrm{NaN_3}} = n_{\mathrm{N_2}} \frac{2}{3} = 2.68\ \mathrm{mol} \times \frac{2}{3} = 1.78\ \mathrm{mol}$$

Step 3. Convert the number of moles of NaN_3 into mass:

Molar mass (g/mol) of NaN_3

$$m_{\mathrm{NaN_3}} = M_{\mathrm{NaN_3}} \times n_{\mathrm{NaN_3}} = 65.0\ \mathrm{g \cdot mol^{-1}} \times 1.78\ \mathrm{mol} = 116\ \mathrm{g}$$

Many Pressure Units

1 **torr** = 1 mmHg
⇒ pressure needed to raise a column of mercury (Hg) by 1 mm

1 **atm** = 760 torr
⇒ average atmospheric pressure at sea level (in dry conditions) at 0 ^{o}C

1 **atm** = 101 325 **Pa**
⇒ 1 atm EQUALS exactly 101 325 Pa (or $N \cdot m^{-2}$)

1 **bar** = 100 000 Pa
⇒ used as the "*standard*" pressure in thermodynamics.

Standard vs Normal Conditions

1)"Standard" Temperature/Pressure, or STP: 273.15 K (0°C) and 1 bar

2)"Normal" Temperature/Pressure, or NTP: 293.15 K (20°C) and 1 atm

Dalton's Law of Partial Pressures

When two gases, say A and B, are mixed together,

the **total pressure** of the mixture can be separated into a **partial pressure** due to gas A and a **partial pressure** due to gas B.

Dalton's Law: $P_{tot} = \sum_i P_i$

total pressure = sum of the pressures of individual components

Dalton's Law of Partial Pressures

A **Partial Pressure** is simply the pressure that a gas would exert if it were the only gas in the SAME container. It is directly proportional to the **mole fraction** of that component in the mixture.

For one gas: $$P_i = \frac{n_i RT}{V}$$

For the mixture: $$P_{tot} = P_1 + P_2 + P_3 \cdots = \left(n_1 + n_2 + n_3 \cdots\right)\frac{RT}{V} = \frac{n_{tot} RT}{V}$$

Molar fraction: $$\frac{P_i}{P_{tot}} = \frac{n_i}{n_{tot}} = x_i \quad \Rightarrow \quad P_i = x_i P_{tot}$$

The partial pressure of component i = The molar fraction times the total pressure"

molar fraction of component *i*

Dalton's Law: Typical Problem 1

Three gases are mixed:

- 1 L O_2 at 2 atm
- 2 L N_2 at 1 atm
- 2 L He at 2 atm

If the total volume is 5 L, what is the final pressure?

Total pressure is a sum of partial pressures: $P_{tot} = P_{O_2} + P_{N_2} + P_{He}$

For each species, partial pressures are given by the change in volume:

$$P_{final}V_{final} = nRT = P_{initial}V_{initial} \quad \Rightarrow \quad P_{final} = P_{initial}\frac{V_{initial}}{V_{final}}$$

Final Partial pressures of the three gases:

$$P_{O_2} = 2\ \text{atm} \times \frac{1\ \text{L}}{5\ \text{L}} = 0.4\ \text{atm}$$

$$P_{N_2} = 1\ \text{atm} \times \frac{2\ \text{L}}{5\ \text{L}} = 0.4\ \text{atm}$$

$$P_{He} = 2\ \text{atm} \times \frac{2\ \text{L}}{5\ \text{L}} = 0.8\ \text{atm}$$

$$P_{tot} = P_{O_2} + P_{N_2} + P_{He}$$

$$P_{tot} = (0.4 + 0.4 + 0.8)\ \text{atm} = 1.6\ \text{atm}$$

Dalton's Law: Problem 2 with limiting reagents

$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$$

4 L NO at 0.5 atm is mixed with 2 L O_2 at 1 atm and constant T. What is the final pressure?

The final total pressure will be:
the sum of the partial pressures of the reactant left and of the product formed.

First, calculate how much of each reactant we have in the beginning.

Note: because numbers of moles are proportional to pressure (if V and T are constant), *we can always use pressure in stoichiometry like moles of a gas.*

	$2NO_{(g)}$	+	$O_{2(g)}$	$\longrightarrow$	$2NO_{2(g)}$
initial: (After mixing Before Reacting):	$0.5 \text{ atm} \times \frac{4 \text{ L}}{6 \text{ L}} = \frac{1}{3} \text{ atm}$		$1.0 \text{ atm} \times \frac{2 \text{ L}}{6 \text{ L}} = \frac{1}{3} \text{ atm}$		0 atm

Dalton's Law: Problem 2 with limiting reagents

4 L NO at 0.5 atm is mixed with 2 L O_2 at 1 atm.
What is the final pressure?

$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$$

Everytime one O_2 reacts, two NO disappear: since we have equal amounts of the two, clearly NO will be all consumed and some O_2 will be left (i.e., NO is the limiting reactant):

	$2NO_{(g)}$	+	$O_{2(g)}$	$\longrightarrow$	$2NO_{2(g)}$
Initial after mixing:	$\frac{1}{3}$ atm		$\frac{1}{3}$ atm		0 atm
		ratio NO/O₂		***ratio NO/NO₂***	
used/formed:	$-\frac{1}{3}$ atm		$-\left(\frac{1}{2}\right)\times\frac{1}{3}$ atm		$+\left(\frac{1}{1}\right)\times\frac{1}{3}$ atm
final:	0 atm		$\frac{1}{6}$ atm		$+\frac{1}{3}$ atm

Final Total Pressure:

$$P_{tot} = P_{NO} + P_{O_2} + P_{NO_2} = \left(0 + \frac{1}{6} + \frac{1}{3}\right) \text{ atm} = 0.5 \text{ atm}$$

Dalton's Law: Typical Problem 3

Consider a mixture of 40.0 g of He and 40.0 g of O_2 at 2.0 atm. What is the partial pressure of He in this mixture?

Calculate moles of each gas:

$$n_{\mathrm{He}} = \frac{m_{\mathrm{He}}}{M_{\mathrm{He}}} = \frac{40.0\ \mathrm{g}}{4\ \mathrm{g \cdot mol^{-1}}} = 10.0\ \mathrm{mol}$$

$$n_{\mathrm{O_2}} = \frac{m_{\mathrm{O_2}}}{M_{\mathrm{O_2}}} = \frac{40.0\ \mathrm{g}}{32\ \mathrm{g \cdot mol^{-1}}} = 1.25\ \mathrm{mol}$$

Then use Dalton's Law to calculate partial pressure of helium:

$$P_{\mathrm{He}} = x_{\mathrm{He}} \cdot P_{tot} = \frac{n_{\mathrm{He}}}{n_{tot}} \cdot P_{tot} = \frac{10.0\ \mathrm{mol}}{(10.0 + 1.25)\mathrm{mol}} 2.0\ \mathrm{atm} = 1.8\ \mathrm{atm}$$

Note: the partial pressure of oxygen can be calculated the same way, but it's easier to simply see that it must be the remainder of the total pressure: 0.2 atm.

Dalton's Law: Typical Problem 4

A) A 4.0 L vessel contains: 1.0 mole of He, 2.0 moles of N_2, 2.0 moles of H_2 at 10.0 atm. What is the partial pressure of nitrogen in the vessel?

B) An additional 3.0 moles of nitrogen are added to the flask (T constant). What is the new partial pressure of nitrogen? what is the total pressure?

Dalton's Law: Typical Problem 4

A) A 4.0 L vessel contains: 1.0 mole of He, 2.0 moles of N_2, 2.0 moles of H_2 at 10.0 atm. What is the partial pressure of N_2 in the vessel?

Then use Dalton's Law to calculate the partial pressure of N_2:

$$n_{tot} = (1.0 + 2.0 + 2.0)\ \text{mol} = 5.0\ \text{mol}$$

$$P_{N_2} = x_{N_2} \cdot P_{tot} = \frac{2.0\ \text{mol}}{5.0\ \text{mol}} \cdot 10.0\ \text{atm} = 4.0\ \text{atm}$$

Dalton's Law: Typical Problem 4

A) A 4.0 L vessel contains: 1.0 mol of He, 2.0 moles of N_2, 2.0 moles of H_2 at 10.0 atm. What is the partial pressure of N_2 in the vessel?

B) An additional 3.0 moles of N_2 are added to the flask (T constant). What is the new partial pressure of N_2? What is the total pressure?

After the addition of N_2, the temperature and volume remain the same.

Before the addition: $n_{tot1} = n_{He} + n_{N2} + n_{H2}$ = 1 mol + 2 mol + 2 mol = 5 mol

After the addition: $n_{tot2} = n_{He} + n_{N2} + n_{H2}$ = 1 mol + 5 mol + 2 mol = 8 mol

Before the addition: $n_{tot\,1}RT = P_{tot\,1}V$

After the addition: $n_{tot\,2}RT = P_{tot\,2}V$

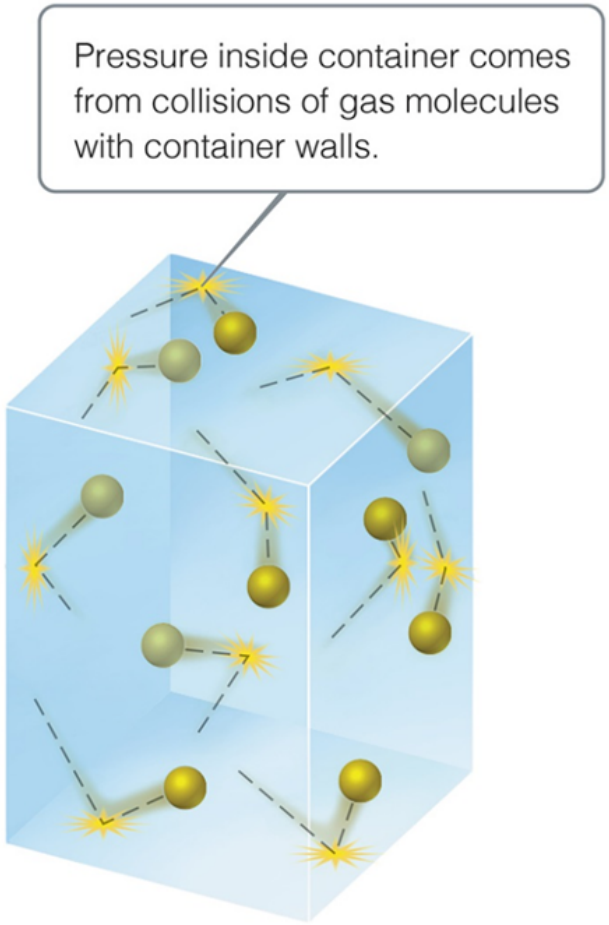
$$\frac{n_{tot\,1}}{n_{tot\,2}} = \frac{P_{tot\,1}}{P_{tot\,2}}$$

$$P_{tot\,2} = P_{tot1}\frac{n_{tot\,2}}{n_{tot1}} = 10.0\ \text{atm}\,\frac{8.0\ \text{mol}}{5.0\ \text{mol}} = 16.0\ \text{atm}$$

$$P_{N_2} = x_{N_2} \cdot P_{tot} = \frac{5.0\ \text{mol}}{8.0\ \text{mol}} \cdot 16.0\ \text{atm} = 10.0\ \text{atm}$$

10.5 Kinetic-Molecular Theory of Gases

- The kinetic/molecular Theory of gases *rationalizes* gas behavior.



Kinetic molecular Theory of Gases

Summary: Based on ideal gas behavior.

1. Gas molecules are in **constant random, rapid motion**, colliding with each other and the walls of the container.

2. **Collisions occur with no loss of energy**. If that happened, the gas would cool down over time as energy is lost.

3. Gas molecules are **very far apart** compared to their size.
   Ideal gas assumption is that they have 0 volume.

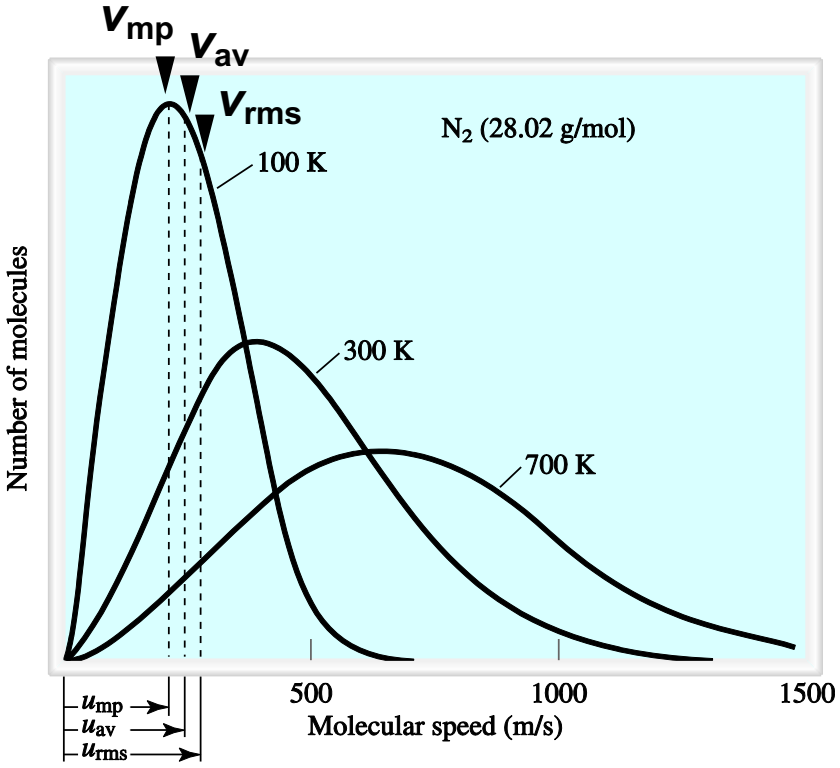
4. **Attraction/repulsion** between molecules is **weak and ineffective**.
   Ideal gas assumption is that there is NO attraction or repulsion.
   Basically, ideal gas molecules/atoms are billiard balls with 0 volume.

5. The **average kinetic energy** of the collection of gas molecules **depends only on**, and is proportional to, **the absolute temperature** (K).

Kinetic Theory of Gases

There is always a **distribution** of molecular speeds - some molecules are moving fast, while others are moving slowly.

Maxwell-Boltzmann Distribution describes the probability that a random gas molecule has a certain speed:



The root-mean-square speed, v_{rms} :

$$< v^2 >^{1/2} = v_{rms} = \sqrt{\frac{3RT}{M}}$$

- It is slightly bigger than the average speed, v_{av}.
- The speed at which the molecule has an average kinetic energy.

The average speed, v_{av} :

$$< v > = v_{av} = \sum_i p_i \cdot v_i$$

$p_i = fraction\ of\ gas\ particles\ having\ velocity\ v_i$

The most probable speed, v_{mp}:

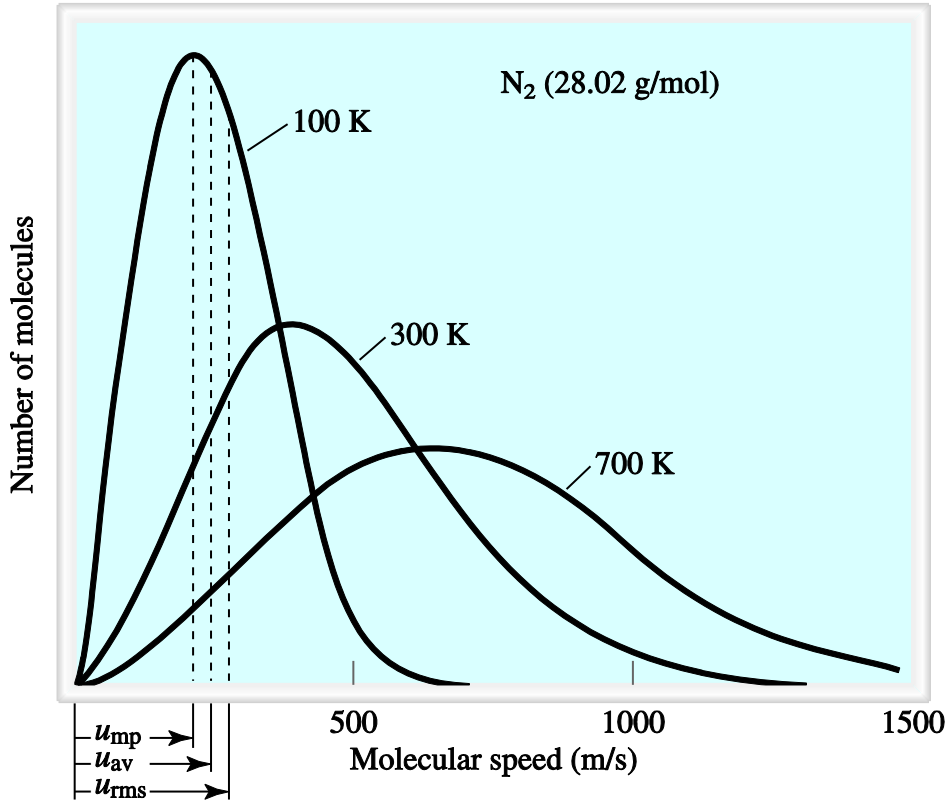
The speed at which the probability is the highest.

Kinetic Theory of Gases

- **Higher temperature → Higher kinetic energy→ Higher speed**:

  Curves shift to the right. Note that the curves also become **broader**,

- A wider *range* of speeds. - **height of the peak decreases**
  - M*ore possibilities for the speed*
  - *Less probability for each possibility*
  - *But why??*



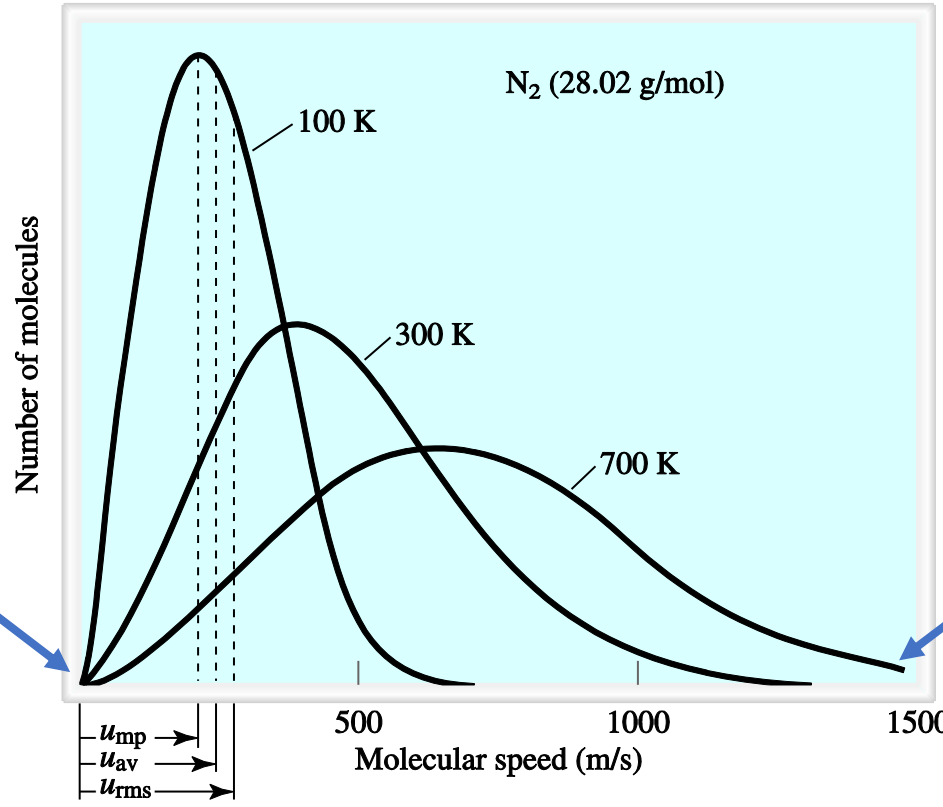
Kinetic Theory of Gases

- **Higher temperature → Higher kinetic energy→ Higher speed**:

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- A wider *range* of speeds. - **height of the peak decreases**
  - *More possibilities for the speed*
  - *Less probability for each possibility*
  - *But why??*

Note, graph is three different Temperatures, one gas



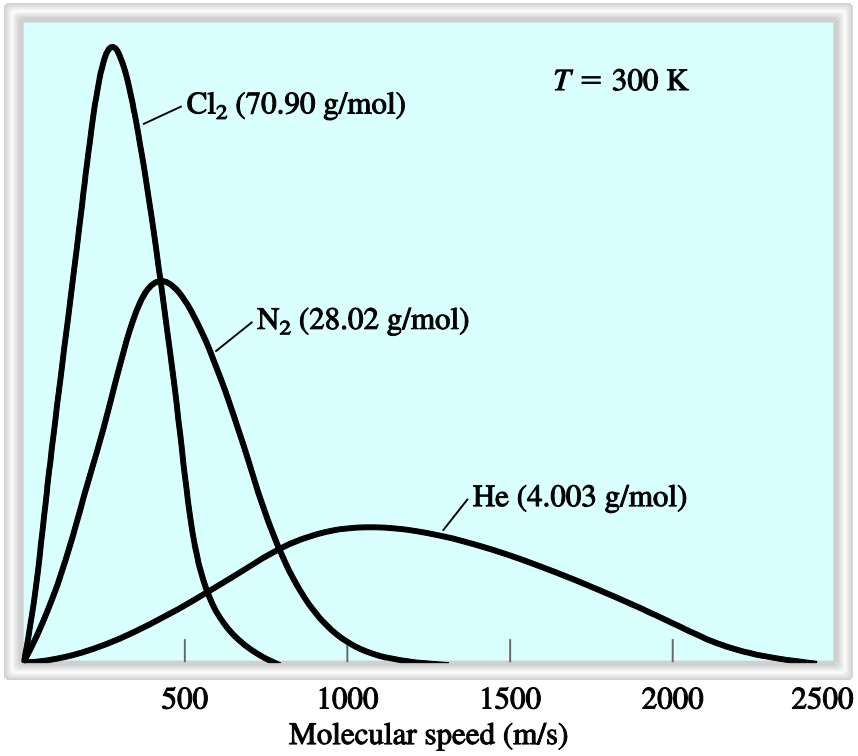
Lowest speed cutoff
Can't go slower than 0

Can always go faster

Kinetic Theory of Gases

Decreasing the mass of the particles INCREASES the speed of the molecules: on a Maxwell-Boltzmann plot, the curves shift to the right

Note, graph is *one gas three temperatures.*



The root-mean-square speed, v_{rms} :

$$< v^2 >^{1/2} = v_{rms} = \sqrt{\frac{3RT}{M}}$$

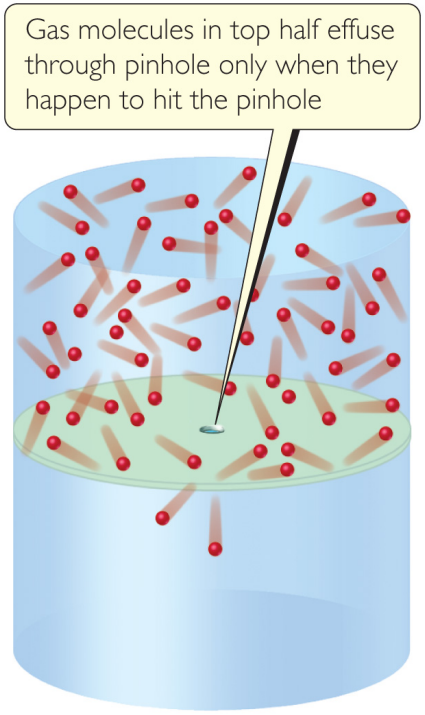
Although lighter molecules have higher speeds, each collision has a less impact on pressure because their mass is smaller.

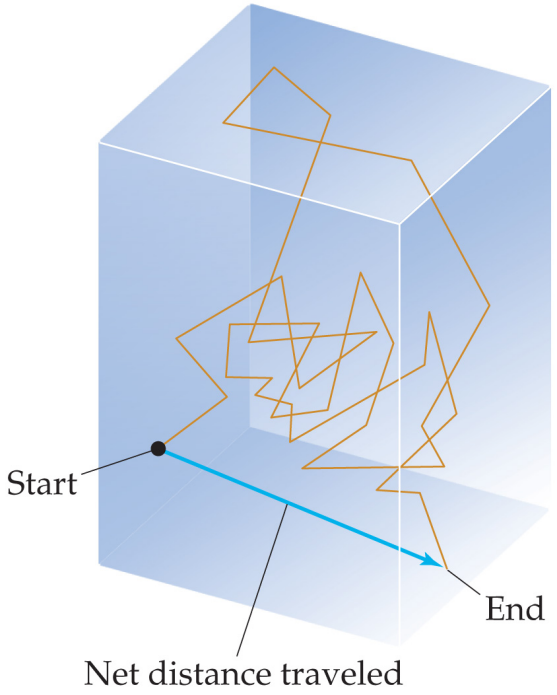
Effusion & Diffusion

Effusion is the escape of gas molecules through a tiny hole into an evacuated space.

"Tiny" means only one molecule at a time is expected to go through.

Diffusion is the spread of one substance throughout a space or a second substance.





Graham's law off effusion and diffusion

The faster molecules move, the faster they diffuse or effuse:

remember speed:

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

$$\frac{v_{rms_1}}{v_{rms_2}} = \sqrt{\frac{\frac{3RT}{M_1}}{\frac{3RT}{M_2}}} = \sqrt{\frac{M_2}{M_1}} = \frac{rate_1}{rate_2}$$

ratio of rates of effusion:

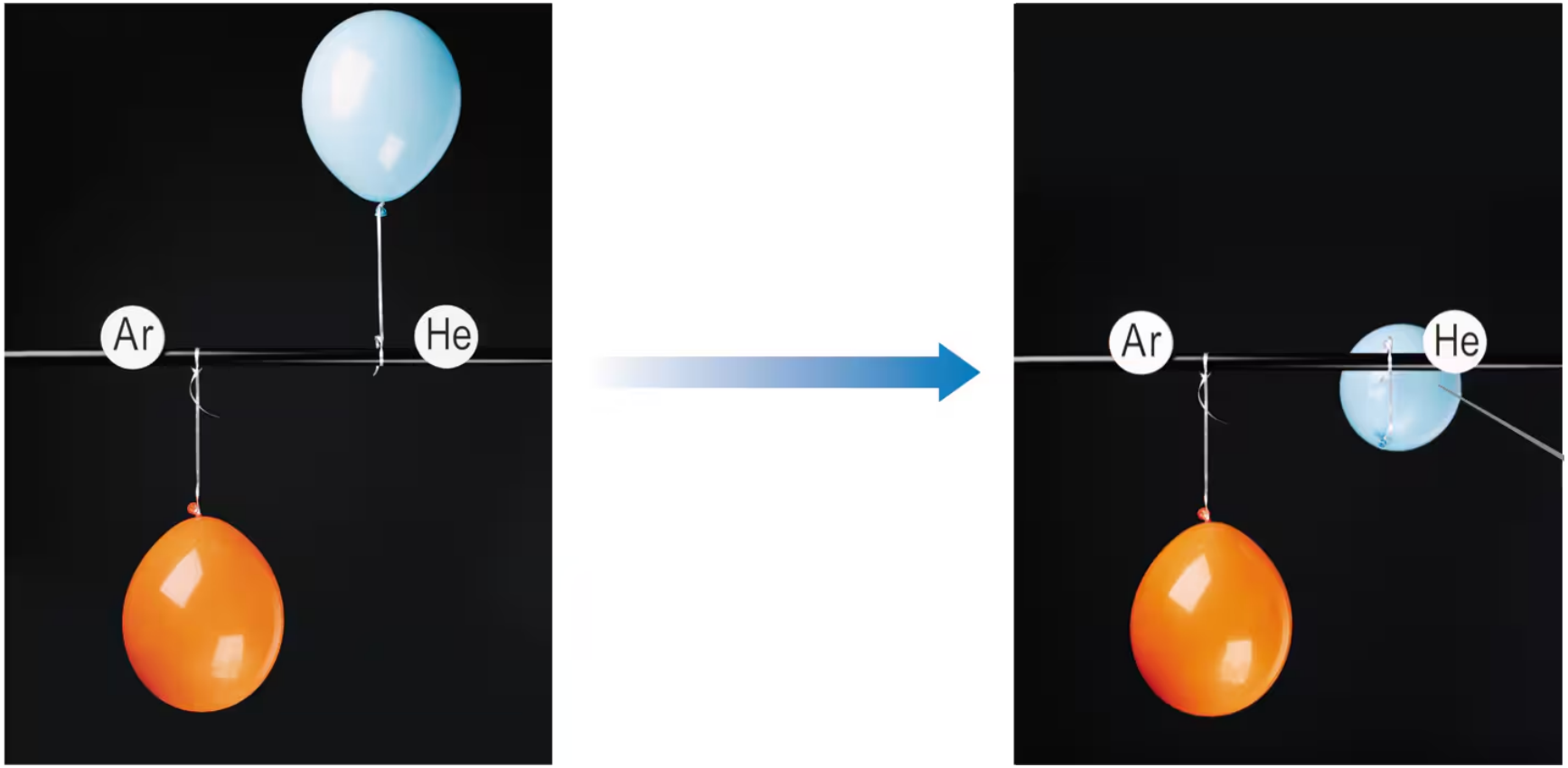
$$\frac{rate_1}{rate_2} = \sqrt{\frac{M_2}{M_1}}$$

Example: H_2 : M = 2

O_2 : M = 32

$(32/2)^{1/2}$ =4 . Hydrogen diffuses 4 times faster than oxygen.

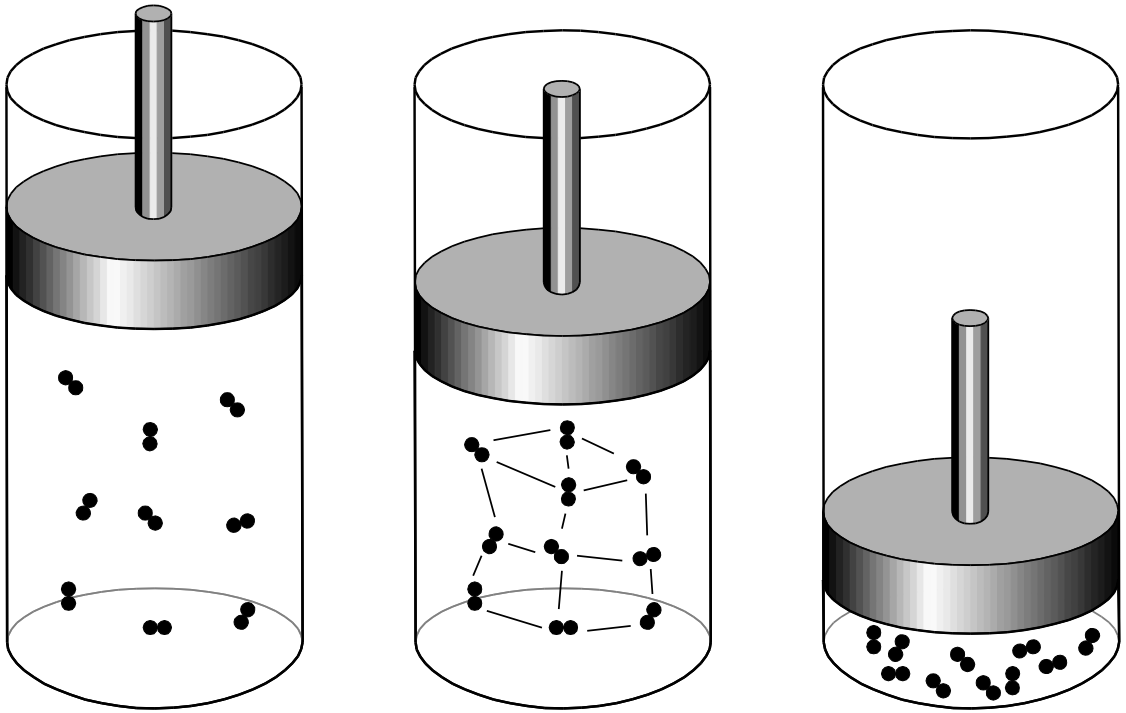
Effusion example



Real Gases

Ideal Gas
Size = zero
attraction = zero

Real Gas
Size ≠ zero
attraction > zero



almost zero pressure
ideal behavior
Z = zero

low pressure
attractive forces predominate
Z < zero

high pressure
repulsive forces predominate
Z > zero

Almost zero pressure
Ideal behavior
Molecules never touch
Volume taken up by gas
Too small to matter

Low pressure
Attractive forces dominate.
Molecules "see" each other
Enough to attract.
Empty space still way more than gas volume

High pressure
Repulsive forces dominate.
Gas volume finally matters.

Compressibility Factor (*Z*)

A measure of the deviation from an ideal gas

The larger *Z* is, the harder the gas is to compress.

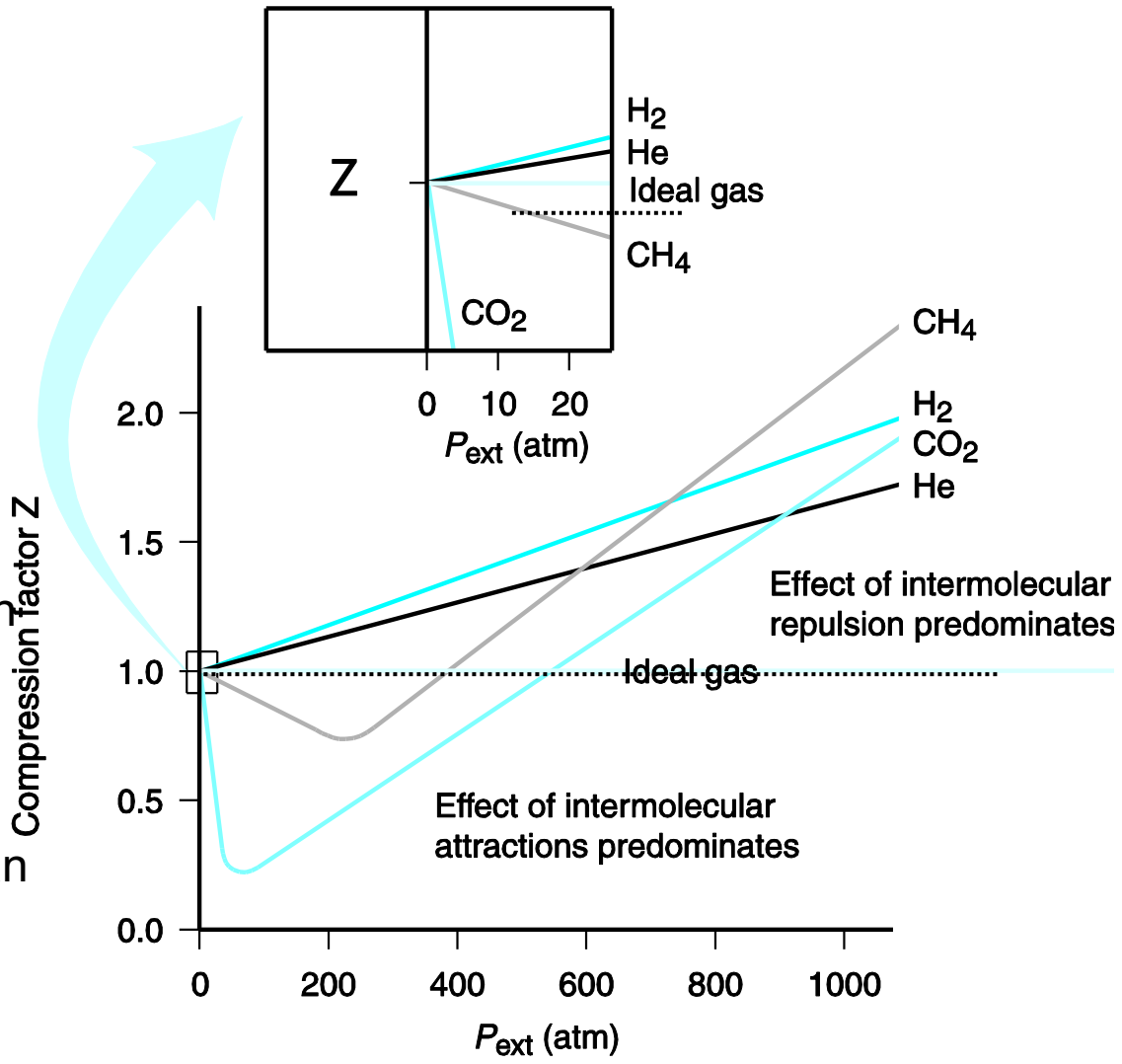
$$Z = \frac{P_{obs}V}{nRT}$$

$$= 1 \ (\text{ideal gas})$$

$$\neq 1 \ (\text{real gas})$$

$Z > 1$ Pressure is ***bigger*** than ideal gas (repulsion dominates)

$Z < 1$ Pressure is ***smaller*** than ideal gas (attraction dominates)



Compressibility Factor (*Z*)

P_{obs} (or P_{real}) is the observed pressure when you have *n* moles of a REAL gas in a volume *V* at a temperature *T*.

$$Z = P_{real} \times \frac{V}{nRT}$$

It is different than P_{ideal} , the calculated pressure that *n* moles of an IDEAL gas would have when the volume is *V* and the temperature is *T*.

$$P_{ideal} = \frac{nRT}{V}$$

If we put P_{ideal} into the equation above we then get:

$$Z = \frac{P_{real}}{P_{ideal}}$$

Z > 1 is when the pressure is larger than ideal gas,

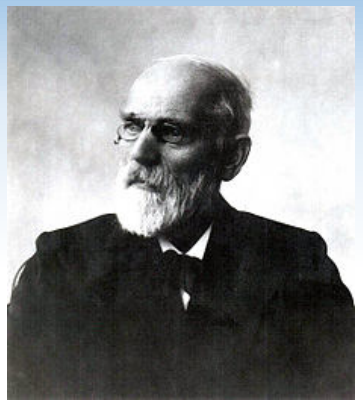
Z < 1 is when the pressure is less than ideal gas.

van der Waals Equation

Accounts for the attraction/repulsion between molecules

Accounts for the non-zero size of the molecules

$$\left[P_{obs} + a\left(\frac{n}{V}\right)^2\right] \times \left(V_{obs} - nb\right) = nRT$$



Johannes van der Waals

1837-1923
Nobel prize in physics (1910)
His work on the equation of state of gases and liquids

We need two parameters, *a* and *b*, to describe real gases. These change every time you look at a different gas: real gases each have their own individual behavior (more or less attractive, more or less big).

UNITS: $a : \text{atm} \cdot \text{L}^2 \cdot \text{mol}^{-2}$ $\quad b : \text{L} \cdot \text{mol}^{-1}$

The van der Waals equation can describe real gases

$$P \times V = nRT$$ when a = 0 and b = 0.

van der Waals Equation

TABLE 27.1 The values of the van der Waals constants *a* and *b* for some common gases.

Gas	a (L^2 atm mol^{-2})	b (L mol^{-1})
ideal gas	0	0
helium	0.034	0.0237
neon	0.211	0.0171
hydrogen	0.246	0.0266
argon	1.35	0.0322
oxygen	1.37	0.0318
nitrogen	1.39	0.0391
methane	2.25	0.0428
krypton	2.32	0.0398
carbon dioxide	3.64	0.0427
xenon	4.19	0.0511
ammonia	4.22	0.0371
hydrogen sulfide	4.49	0.0429
water vapor	5.46	0.0305
ethane	5.56	0.0638
chlorine	6.49	0.0562

Accounts for the attraction between molecules

Accounts for the non-zero size of the molecules

$$\overbrace{\left[P_{obs} + a\left(\frac{n}{V}\right)^2\right]}^{\text{attraction}} \times \overbrace{\left(V_{obs} - nb\right)}^{\text{size}} = nRT$$

- *b* is much smaller than *a*.
- *a* varies much more than *b*.

The effects of attraction are more important than the effect of size.

van der Waals Equation

Example: Exactly one liter of hydrogen at 0^{o}C contains 4.500 grams of hydrogen at 51.40 atm (observed pressure).

a) Calculate the pressure assuming that H_2 behaves ideally;

b) Calculate the pressure using the van der Waals equation (a = 0.246 atmL^{2}mol^{-2}, b = 0.0266 Lmol^{-1})

c) Compare both calculated pressures with the observed value.

van der Waals Equation

Example: Exactly 1 liter of hydrogen at 0°C contains 4.500 grams of hydrogen at 51.40 atm (observed pressure).

a) Calculate the pressure assuming that H_2 behaves ideally

$$n = \frac{m_{H_2}}{M_{H_2}} = \frac{4.500\ \text{g}}{2.016\ \text{g}\cdot\text{mol}^{-1}} = 2.232\ \text{mol}$$

$$P = \frac{nRT}{V}$$

$$= \frac{2.232\ \text{mol} \times 0.08206\ \text{atm}\cdot\text{L}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \times 273.15\ \text{K}}{1\ \text{L}}$$

$$= 50.03\ \text{atm}$$

van der Waals Equation

Example: Exactly 1 liter of hydrogen at 0°C contains 4.500 grams of hydrogen at 51.40 atm (observed pressure).

b) Calculate the pressure using the van der Waals equation (a = 0.246 atm L^2 mol^{-2}, b = 0.0266 L mol^{-1})

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

$$V - nb = 1.000\ \text{L} - 2.232\ \text{mol} \times 0.0266\ \text{L} \cdot \text{mol}^{-1} = 0.9406\ \text{L}$$

$$a\left(\frac{n}{V}\right)^2 = 0.246\ \text{atm} \cdot \text{L}^2 \cdot \text{mol}^{-2} \left(\frac{2.232\ \text{mol}}{1.000\ \text{L}}\right)^2 = 1.226\ \text{atm}$$

$$P = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2 = \frac{2.232\ \text{mol} \times 0.08206\ \text{atm} \cdot \text{L} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 273.15\ \text{K}}{0.9406\ \text{L}} - 1.226\ \text{atm}$$

$$= 51.96\ \text{atm}$$

van der Waals Equation

Example: Exactly 1 liter of hydrogen at 0°C contains 4.500 grams of hydrogen at 51.40 atm (observed pressure).

c) Compare both calculated pressures with the observed value.

$$P_{obs} = 51.40 \text{ atm}$$

$$P_{ideal} = 50.03 \text{ atm} \quad (\sim 3\% \text{ off})$$

$$P_{vdW} = 51.90 \text{ atm} \quad (< 1\% \text{ off})$$

Conclusions:

H_2 behaves almost like an ideal gas at the conditions above (0°C and 51.4 atm) (only 3% error).

But note: Works even better at lower P. (less n/V, less n)

Nevertheless, van der Waals equation does a better job at predicting the pressure of H_2 than the ideal gas law.

Where's the difference? (repulsion or size??) what do you think?

van der Waals Equation

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Nevertheless, van der Waals equation does a better job at predicting the pressure of H_2 than the ideal gas law.

Where's the difference? (repulsion or size??) what do you think?

$$Z = \frac{P_{obs}}{P_{ideal}} = 1.007$$

$Z > 1$ for H_2, the *repulsion* from the *size* of the molecules (*b* parameter) matters more than attraction (stickiness) (*a*).