

WILEY

Chapter 10
Properties of Gases

Chemistry, 7th Edition
International Student Version
Brady/Jespersen/Hyslop

Chapter in Context

- Describe the properties of gases at the everyday and molecular levels
- Explain the measurement of pressure using barometer and manometers
- Use the gas laws of Dalton, Charles, Gay-Lussac, and the combined gas law
- Perform stoichiometric calculations using the gas laws and Avogadro's principle

Chapter in Context, cont'd

- Apply the ideal gas law and explore how it incorporates the other gas laws
- Use Dalton's law of partial pressures
- Study the collection of gas over water
- Use the kinetic theory of gases to explain gas laws at a molecular level
- Explain the physical significance of the terms in the van der Waals equation of state

Properties of Common Gases

Common characteristics of gases

- Offer little physical resistance
- Can be compressed or expand (e.g., car tires)
- Exert a pressure (e.g., balloons)
- Pressure depends on amount of confined gas
- Fill a container completely (glass of water can be half-full, but gas expands to fill its container)
- Mix freely (e.g., air is a mixture, perfumes mix)
- Pressure rises and falls with temperature (e.g., aerosol cans)

Molecular Model of Gases

Observations suggest

- A lot of space between molecules
- Molecules are moving at high speeds
- Molecules collide with walls of the container
- Molecules move faster at higher temperatures and slower at lower temperatures

Your Turn!

Based on the previous descriptions, which analogy is likely the best one for visualizing the behavior of gases at the molecular level? In other words, gases are like:

- A. A swamp with a lot of animals crawling around
- B. Concrete being poured
- C. Ping pong balls bouncing around in a plexiglass container
- D. A bowl of jiggling Jell-O

Properties of Common Gases

- Despite wide differences in chemical properties, **all** gases more or less obey the same set of **physical properties**

Four Physical Properties of Gases

- Inter-related
 1. Pressure (**P**)
 2. Volume (**V**)
 3. Temperature (**T**)
 4. Amount = moles (**n**)

Pressure: Measurement and Units^{10.2}

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

- Pressure is force per unit area
- Earth exerts gravitational force on everything with mass near it
- **Weight**
 - Measure of gravitational **force** that **earth** exerts on objects with mass
- What we call **weight** is gravitational force acting on object

Force vs. Pressure

- Consider a woman wearing flat shoes vs. high heels
 - Weight of woman is same = 120 lbs
 - Pressure on floor differs greatly

Shoe	Area	Pressure
Flat	10 in. × 3 in. = 30 in. ²	$P = \frac{120 \text{ lbs}}{30 \text{ in.}^2} = 4 \text{ psi}$
High Heels	0.4 in × 0.4 in = 0.16 in. ²	$P = \frac{120 \text{ lbs}}{0.16 \text{ in.}^2} = 750 \text{ psi}$

Why flight attendants do not wear high heels!

Ways to Measure Pressure

- **Atmospheric Pressure**

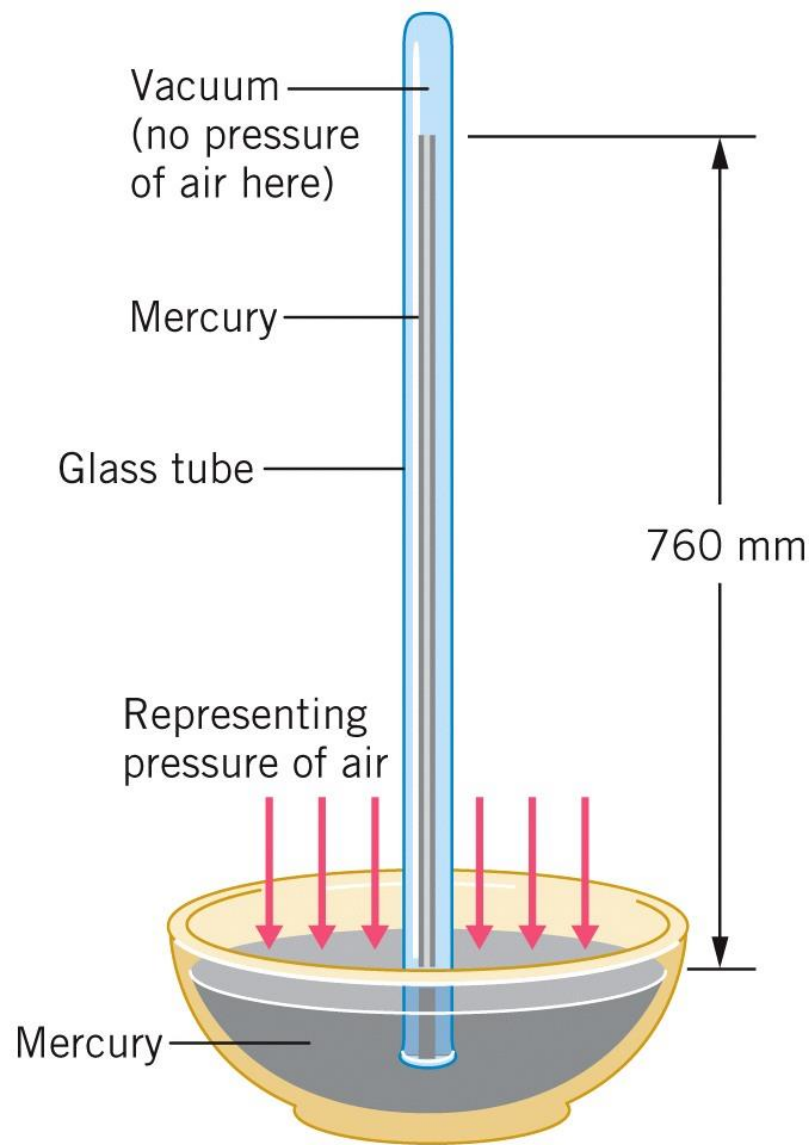
- Resulting force per unit area
- When earth's gravity acts on molecules in air
- Pressure due to air molecules colliding with object

- **Barometer**

- Instrument used to measure atmospheric pressure

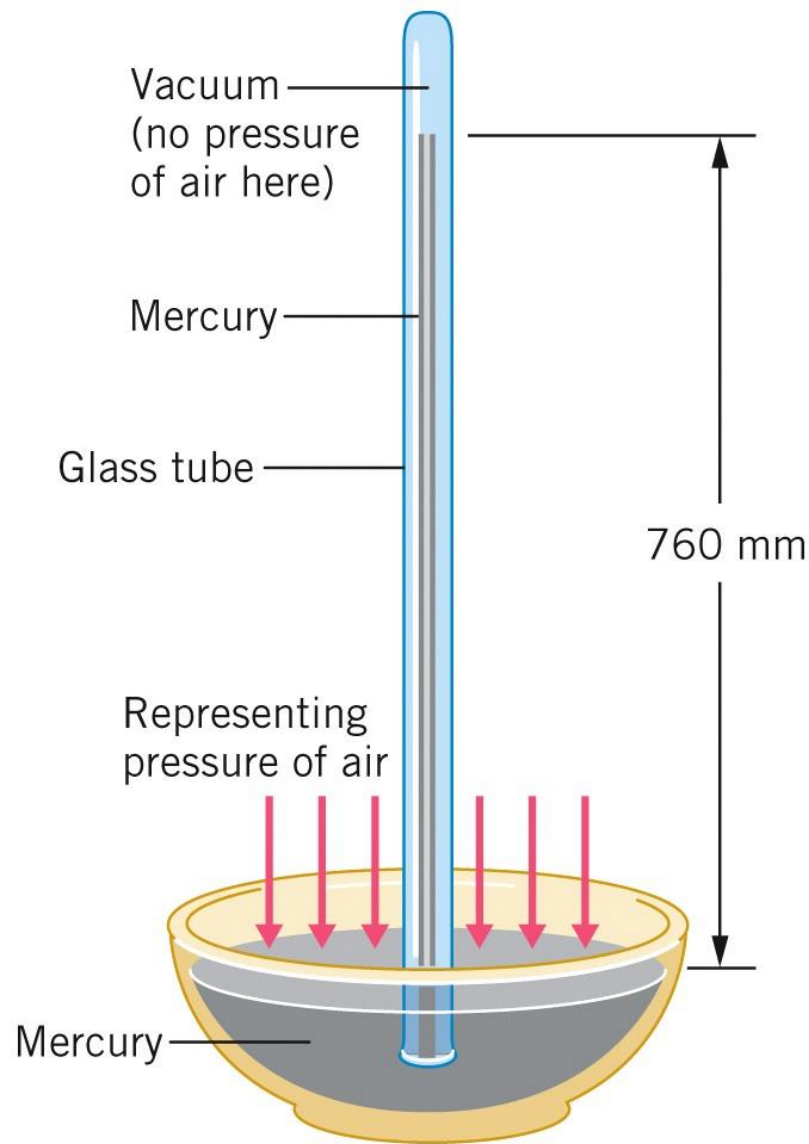
Torricelli Barometer

- Simplest barometer
- Tube that is 80 cm in length
- Sealed at one end
- Filled with mercury
- In dish filled with mercury



Torricelli Barometer

- Air pressure
 - Pushes down on mercury
 - Forces mercury up tube
- Weight of mercury in tube
 - Pushes down on mercury in dish
- When two forces balance
 - Mercury level stabilizes
 - Read atmospheric pressure

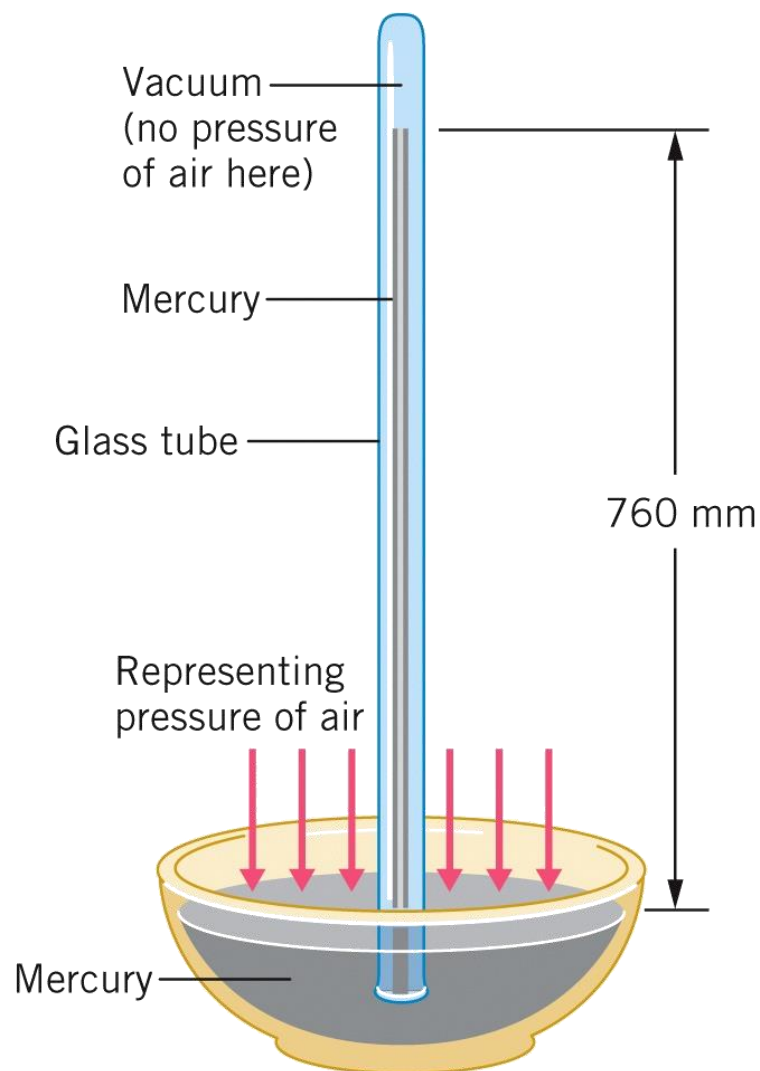


Torricelli Barometer

- If air pressure is high
 - Pushes down on mercury in dish
 - Increase in level in tube
- If air pressure is low
 - Pressure on mercury in dish less than pressure from column
 - Decrease level in tube

Result

- Height of mercury in tube is the atmospheric pressure



Standard Atmospheric Pressure

- Typical range of pressure for most places where people live
730 to 760 mm Hg
- Top of Mt. Everest
Air pressure = 250 mm Hg

Standard atmosphere (atm)

- Average pressure at sea level
- Pressure needed to support column of mercury 760 mm high measures at 0 ° C

Units of Pressure

- SI unit for pressure
 - **Pascal = Pa**
 - Very small
 - $1 \text{ atm} = 101,325 \text{ Pa} = 101 \text{ kPa}$
- Other units of pressure
 - An atm too big for most lab work
 - $1.013 \text{ Bar} = 1013 \text{ mBar} = 1 \text{ atm}$
 - $760 \text{ mm Hg} = 1 \text{ atm}$
 - $760 \text{ torr} = 1 \text{ atm}$

At sea level $1 \text{ torr} = 1 \text{ mm Hg}$

Manometers

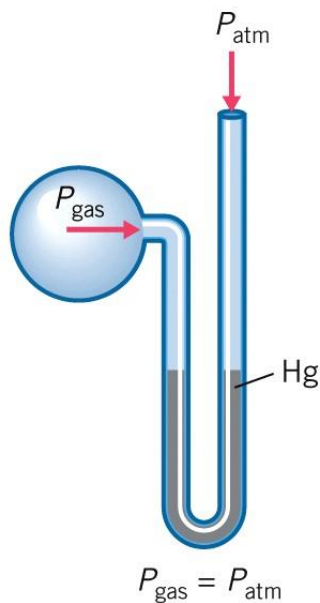
- Used to measure pressure inside closed reaction vessels
 - Pressure changes caused by gases produced or used up during chemical reaction
- **Open-end manometer**
 - U tube partly filled with liquid (usually mercury)
 - One arm open to atmosphere
 - One arm exposed to trapped gas in vessel

Open Ended Manometer

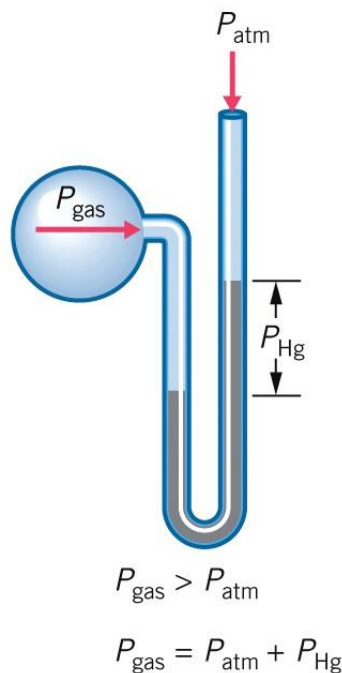
$$P_{\text{gas}} = P_{\text{atm}}$$

$P_{\text{gas}} > P_{\text{atm}}$
 Gas pushes
 mercury **up**
 tube

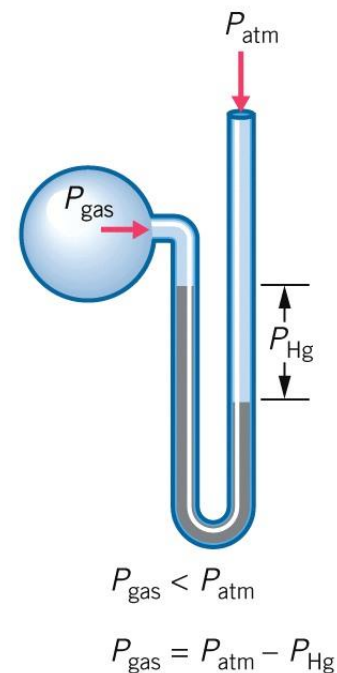
$P_{\text{gas}} < P_{\text{atm}}$
 Atmosphere
 pushes mercury
down tube



(a)



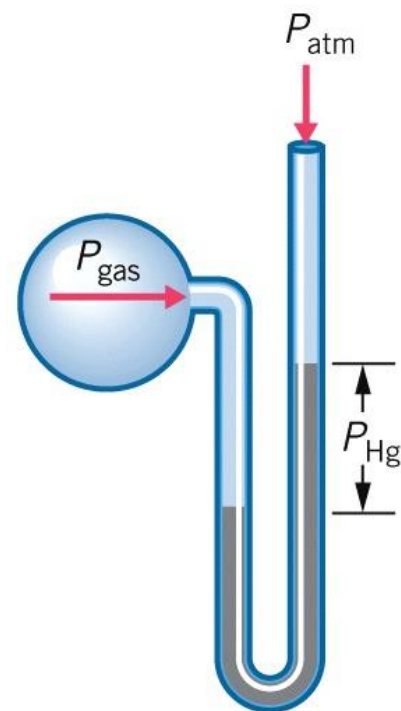
(b)



(c)

Ex. Using Open Ended Manometers

A student collected a gas in an apparatus connected to an open-end manometer. The mercury in the column open to the air was 120 mm higher and the atmospheric pressure was measured to be 752 torr. What was the pressure of the gas in the apparatus?



$$P_{\text{gas}} > P_{\text{atm}}$$

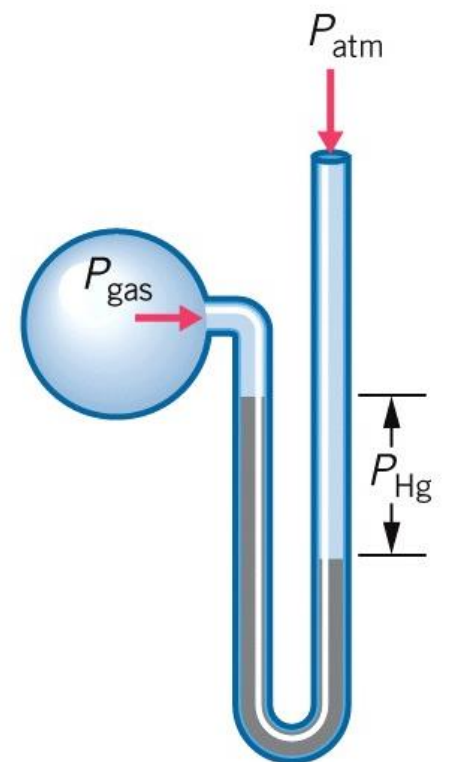
$$P_{\text{gas}} = P_{\text{atm}} + P_{\text{Hg}}$$

This is a case of $P_{\text{gas}} > P_{\text{atm}}$

$$\begin{aligned} P_{\text{gas}} &= 752 \text{ torr} + 120 \text{ torr} \\ &= \mathbf{872 \text{ torr}} \end{aligned}$$

Ex. Using Open Ended Manometers

In another experiment, it was found that the mercury level in the arm of the manometer attached to the container of gas was 200 mm higher than in the arm open to the air. What was the pressure of the gas?



This is a case of $P_{\text{gas}} < P_{\text{atm}}$

$$P_{\text{gas}} = 752 \text{ torr} - 200 \text{ torr}$$

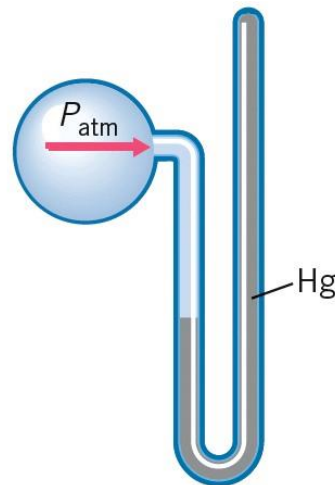
$$= 552 \text{ torr}$$

$$P_{\text{gas}} < P_{\text{atm}}$$

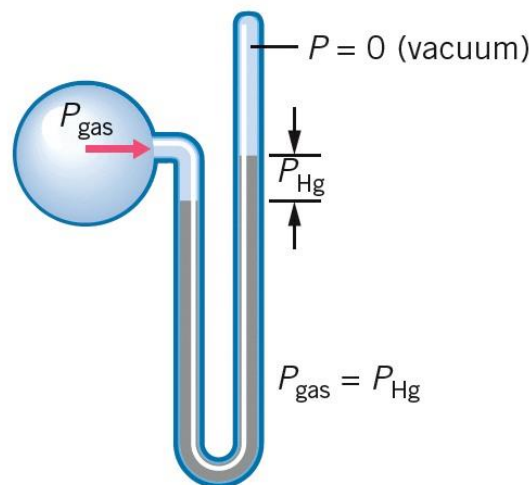
$$P_{\text{gas}} = P_{\text{atm}} - P_{\text{Hg}}$$

Closed-end Manometer

- Arm farthest from vessel (gas) sealed
- Tube filled with mercury
- Then open system to flask and some mercury drains out of sealed arm
- Vacuum exists above mercury in sealed arm



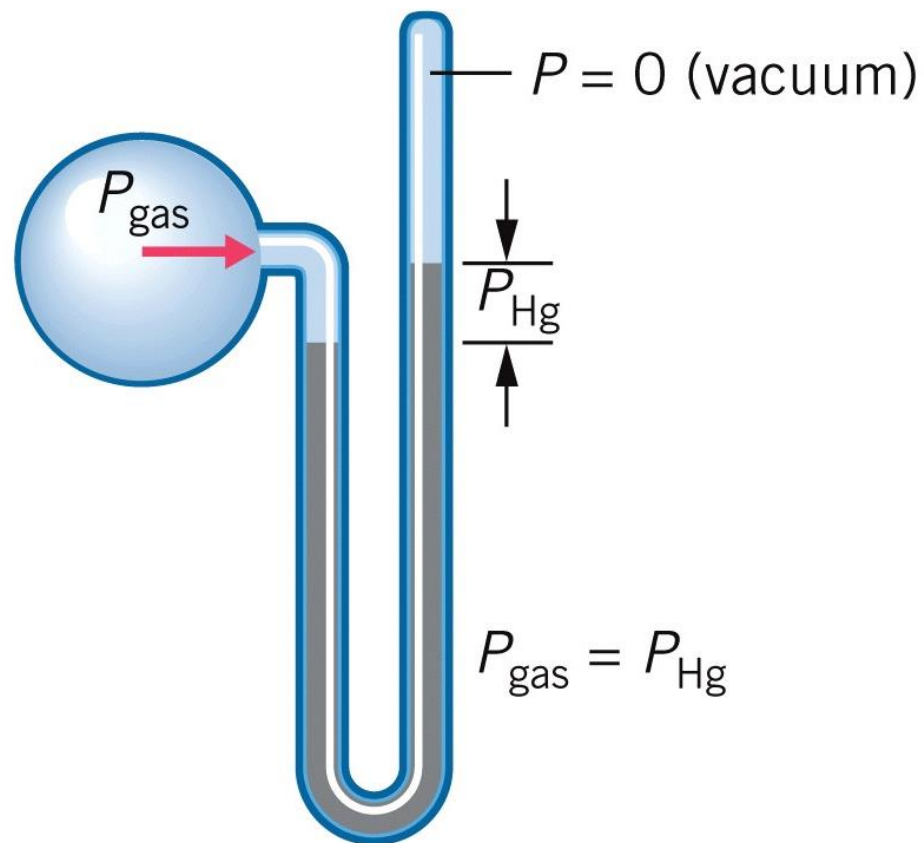
(a)



(b)

Closed-end Manometer

- Level of mercury in arm falls, as not enough pressure in the flask to hold up Hg
- $P_{\text{atm}} = 0$
- $P_{\text{gas}} = P_{\text{Hg}}$
- So directly read pressure



Your Turn!

Gas pressure is measured using a close-ended mercury manometer. The height of fluid in the manometer is 23.7 in. Hg. What is this pressure in atm?

- A. 23.7 atm
- B. 0.792 atm
- C. 602 atm
- D. 1.61 atm

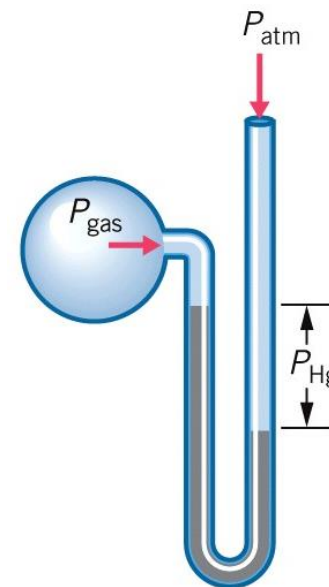
$$23.7 \text{ in. Hg} \cdot \frac{2.54 \text{ cm}}{\text{in}} \cdot \frac{10 \text{ mm}}{\text{cm}} \cdot \frac{1 \text{ atm}}{760 \text{ mm}} = \mathbf{0.792 \text{ atm}}$$

Your Turn!

It was found that the mercury level in the arm of the open-ended manometer attached to the container of gas was 150 mm higher than in the arm open to the air. The external pressure was 780 mmHg. What is the pressure of the gas inside the manometer?

- A. 630 mmHg
- B. 930 mmHg
- C. 0.990 atm
- D. 150 mmHg

$$\begin{aligned}P_{\text{gas}} &< P_{\text{atm}} \\P_{\text{gas}} &= P_{\text{atm}} - P_{\text{Hg}} \\ &= \mathbf{630 \text{ mmHg}}\end{aligned}$$



Comparison of Hg and H₂O

- Pressure of 1 mm column of mercury and 13.6 mm column of water are the same
- Mercury is 13.6 times more dense than water
- Both columns have same *weight* and diameter, so they exert same pressure

Using Liquids Other Than **Mercury** in Manometers and Barometers

- Simple relationship exists between two systems.
- For example, use water ($d = 1.00 \text{ g/mL}$) instead of mercury ($d = 13.6 \text{ g/mL}$) in the tube

In general

$$h_B \cdot d_B = h_A \cdot d_A$$

For converting from
mm Hg to mm H₂O

$$h_{\text{H}_2\text{O}} = \frac{h_{\text{Hg}} \cdot d_{\text{Hg}}}{d_{\text{H}_2\text{O}}}$$

- Use this relationship to convert pressure change in mm H₂O to pressure change in mm Hg

Example: Converting mm Acetone to mm Hg

Acetone has a density of 0.791 g/mL. Acetone is used in an open-ended manometer to measure a gas pressure slightly greater than atmospheric pressure, which is 756.0 mm Hg at the time of the measurement. The liquid level is 20.4 mm higher in the open arm than in the arm nearest the gas sample. What is the gas pressure in torr?

Ex. Converting mm Acetone to mm Hg - Solution

First convert mm acetone to mm Hg

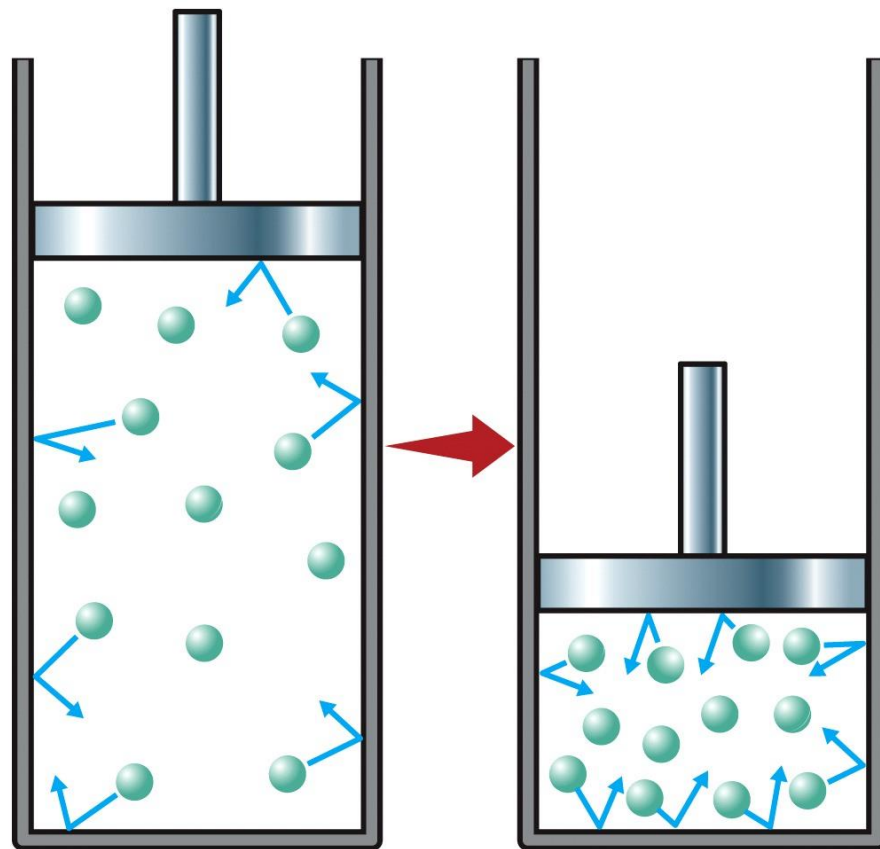
$$h_{\text{Hg}} = \frac{20.4 \text{ mm acetone} \times 0.791 \text{ g/mL}}{13.6 \text{ g/mL}} = 1.19 \text{ mm Hg}$$

Then add P_{Hg} to P_{atm} to get P_{total}

- $P_{\text{gas}} = P_{\text{atm}} + P_{\text{Hg}}$
- $= 756.0 \text{ torr} + 1.19 \text{ torr}$
- $P_{\text{gas}} = 757.2 \text{ torr}$

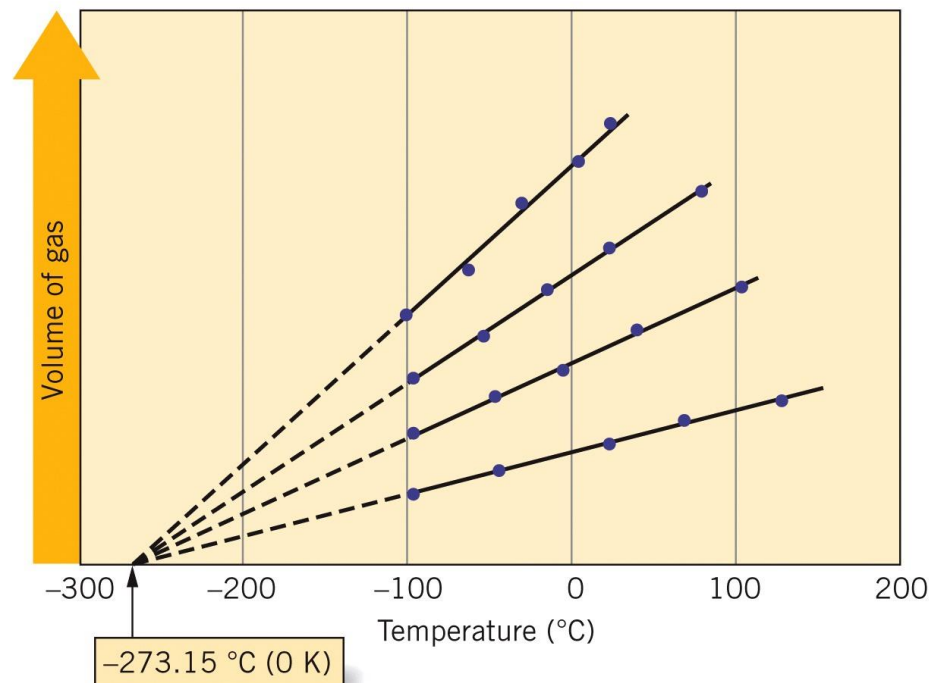
Boyle's Law

- Studied relationship between P and V
- Work done at constant T as well as constant number of moles (n)
- $T_1 = T_2$
- As V decreases, P increases



Charles's Law

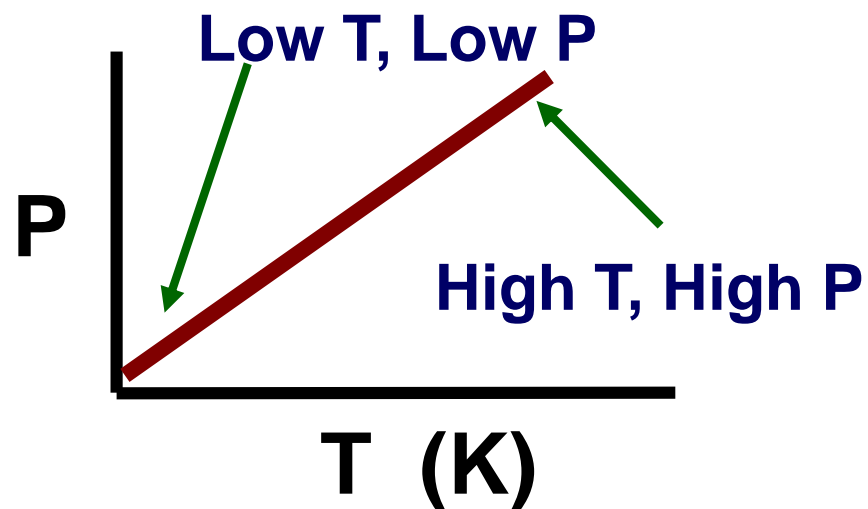
- Charles worked on relationship of how V changes with T
- Kept P and n constant
- Demonstrated V increases as T increases



Gay-Lussac's Law

- Worked on relationship between pressure and temperature
- Volume (V) and number of moles (n) are constant
- P increases as T increases
- This is why we don't heat canned foods on a campfire without opening them!
- Showed that gas pressure is directly proportional to absolute temperature

$$P \propto T$$



Combined Gas Law

- Ratio $\frac{PV}{T}$
- Constant for fixed amount of gas (n)
- $\frac{PV}{T} = C$ for fixed amount of moles
- OR can equate two sets of conditions to give combined gas law

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

Combined Gas Law

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

- All T 's must be in K
- Value of P and V can be any units as long as they are the same on both sides
- Only equation you really need to remember
- Gives all relationships needed for fixed amount of gas under two sets of conditions

How Other Laws Fit into Combined^{10.3} Gas Law

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

Boyle's Law	$T_1 = T_2$	$P_1 V_1 = P_2 V_2$
Charles' Law	$P_1 = P_2$	$\frac{V_1}{T_1} = \frac{V_2}{T_2}$
Gay-Lussac's Law	$V_1 = V_2$	$\frac{P_1}{T_1} = \frac{P_2}{T_2}$

Combined Gas Law

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad 10.3$$

Used for calculating effects of changing conditions

- T in Kelvin
- P and V any units, as long as units cancel

Example: If a sample of air occupies 500. mL at 273.15 K and 1 atm, what is the volume at 85.0 ° C and 560. torr?

$$\frac{\cancel{760 \text{ torr}} \cdot 500. \text{ mL}}{273.15 \cancel{\text{K}}} = \frac{\cancel{560 \text{ torr}} \cdot V_2}{358 \cancel{\text{K}}}$$

$$V_2 = 890. \text{ mL}$$

Ex. Using Combined Gas Law

- What will be the final pressure of a sample of nitrogen gas with a volume of $950. \text{ m}^3$ at 745 torr and $25.0 \text{ }^\circ \text{ C}$ if it is heated to $60.0 \text{ }^\circ \text{ C}$ and given a final volume of 1150 m^3 ?
- First, number of moles is constant even though actual number is not given
- You are given V , P and T for initial state of system as well as T and V for final state of system and must find P_{final}
- This is a clear case for combined gas law

Ex. Using Combined Gas Law

- List what you know and what you don't know
- Convert all temperatures to Kelvin
- Then solve for unknown—here P_2

$$P_1 = 745 \text{ torr}$$

$$P_2 = ?$$

$$V_1 = 950 \text{ m}^3$$

$$V_2 = 1150 \text{ m}^3$$

$$T_1 = 25.0 \text{ }^\circ\text{C} + 273.15 \\ = 298.15 \text{ K}$$

$$T_2 = 60.0 \text{ }^\circ\text{C} + 273.15 \\ = 333.15 \text{ K}$$

$$P_2 = \frac{P_1 V_1 T_2}{T_1 V_2} = \frac{745 \text{ torr} \cdot 950 \text{ m}^3 \cdot 333.15 \text{ K}}{298.15 \text{ K} \cdot 1150 \text{ m}^3}$$

$$P_2 = 688 \text{ torr}$$

Ex. Combined Gas Law

- Anesthetic gas is normally given to a patient when the room temperature is 20.0°C and the patient's body temperature is 37.0°C . What would this temperature change do to 1.60 L of gas if the pressure and mass stay the same?
 - What do we know?
 - P and n are constant
 - So combined gas law simplifies to
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Ex. Combined Gas Law

$$V_1 = 1.60 \text{ L}$$

$$V_2 = ?$$

$$\begin{aligned} T_1 &= 20.0 \text{ }^\circ\text{C} + 273.15 \\ &= 293.15 \text{ K} \end{aligned}$$

$$\begin{aligned} T_2 &= 37.0 \text{ }^\circ\text{C} + 273.15 \\ &= 310.15 \text{ K} \end{aligned}$$

- List what you know and what you don't know
- Convert all temperatures to Kelvin
- Then solve for unknown—here V_2

$$V_2 = \frac{V_1 T_2}{T_1} = \frac{1.60 \text{ L} \cdot 310.15 \text{ K}}{293.15 \text{ K}}$$

$$V_2 = 1.69 \text{ L}$$

Your Turn!

Which units *must* be used in all gas law calculations?

- A. K for temperature
- B. atm for pressure
- C. L for volume
- D. no specific units as long as they cancel

Your Turn!

In order for the combined gas law to be used, what variable must be the same under both sets of conditions?

A. temperature

B. pressure

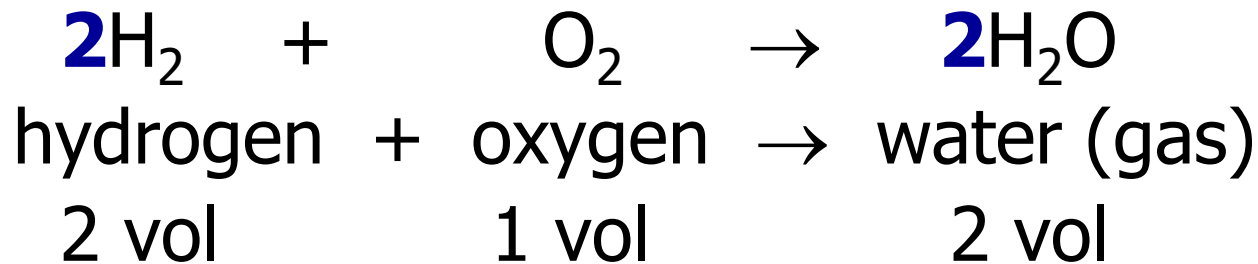
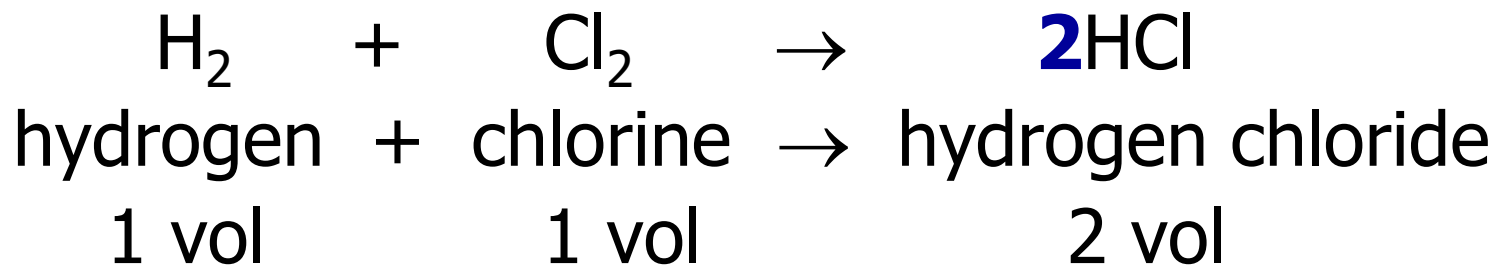
C. volume

D. P , V , and T must all be constant

E. the amount (i.e., number of moles) of gas

Relationships between Gas Volumes

- In reactions in which products and reactants are gases
 - If T and P are constant
 - Simple relationship among volumes



- Ratios of simple, whole numbers

Avogadro's Principle

- When measured at same T and P , equal V 's of gas contain equal number of moles
- Volume of a gas is directly proportional to its number of moles, n
- V is proportional to n (at constant P and T)

	$\text{H}_2(g)$	+	$\text{Cl}_2(g)$	\longrightarrow	$2 \text{HCl}(g)$
Coefficients	1		1		2
Volumes	1		1		2
Molecules	1		1		2 (Avogadro's Principle)
Moles	1		1		2

Your Turn!

If 3 volumes of H₂ are reacted with 1 volume of N₂, how many volumes of ammonia are produced (hint: write the chemical reaction)?

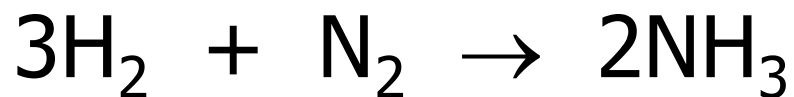
A. 1

B. 2

C. 3

D. 4

E. 5

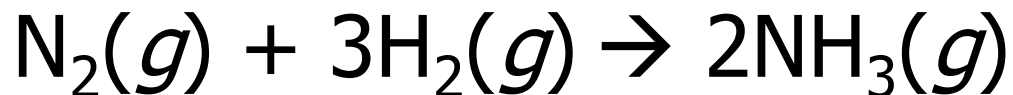


Standard Molar Volume

- Volume of 1 mole gas must be identical for all gases under same P and T
- Standard conditions of temperature and pressure — STP
 - STP = 1 atm and 273.15 K (0.0 °C)
 - Under these conditions
 - 1 mole gas occupies $V = 22.4$ L
 - 22.4 L \equiv standard molar volume

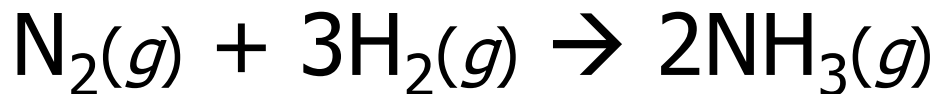
Learning Check:

Calculate the volume of ammonia formed by the reaction of 25 L of hydrogen with excess nitrogen.



$$\frac{25 \cancel{\text{L H}_2}}{1} \cdot \frac{2 \text{ L NH}_3}{3 \cancel{\text{L H}_2}} = 17 \text{ L NH}_3$$

Learning Check:



If 125 L H_2 react with 50.0 L N_2 , what volume of NH_3 can be expected?

$$\frac{125 \cancel{\text{L H}_2}}{1} \cdot \frac{2 \text{ L NH}_3}{3 \cancel{\text{L H}_2}} = 83.3 \text{ L NH}_3$$

$$\frac{50.0 \cancel{\text{L N}_2}}{1} \times \frac{2 \text{ L NH}_3}{1 \cancel{\text{L N}_2}} = 100. \text{ L NH}_3$$

H_2 is limiting reagent 83.3 L

Learning Check:

How many liters of $\text{N}_2(g)$ at 1.00 atm and 25.0 ° C are produced by the decomposition of 150. g of NaN_3 ?

$$2\text{NaN}_3(s) \rightarrow 2\text{Na}(s) + 3\text{N}_2(g)$$

$$\frac{150. \cancel{\text{g NaN}_3}}{1} \cdot \frac{1 \cancel{\text{mol NaN}_3}}{65.0099 \cancel{\text{g}}} \cdot \frac{3 \text{ mol N}_2}{2 \cancel{\text{mol NaN}_3}} = 3.461 \text{ mol N}_2$$

$$\frac{3.461 \cancel{\text{mol N}_2}}{1} \times \frac{22.4 \text{ L}}{1 \cancel{\text{ mol at STP}}} = 77.5 \text{ L}$$

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

$$V_2 = \frac{77.5 \text{ L} \times 298.15 \cancel{\text{K}}}{273.15 \cancel{\text{K}}} = 84.6 \text{ L}$$

Your Turn!

How many liters of SO_3 will be produced when 25 L of sulfur dioxide reacts with 75 L of oxygen? All gases are at STP.

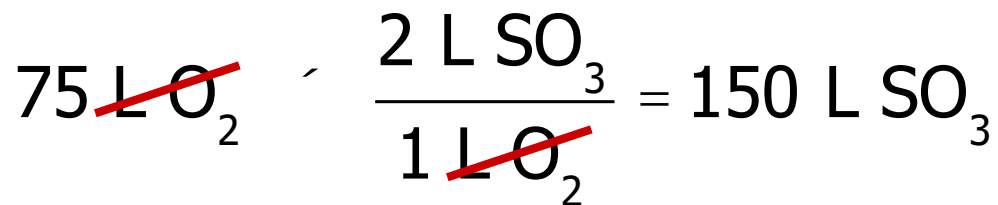
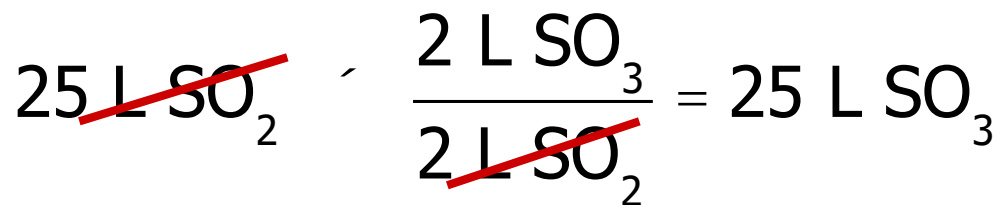
A. 25 L

B. 50 L

C. 100 L

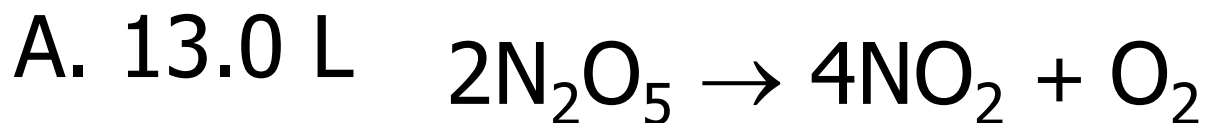
D. 150 L

E. 75 L



Your Turn!

Dinitrogen pentoxide decomposes into oxygen gas and nitrogen dioxide. If all the gases are at the same P and T, what volume of gas is produced when 13.0 L of dinitrogen pentoxide gas completely decompose?



B. 32.5 L

C. 5.20 L So 5 L of gas are produced for every 2 L of N_2O_5 that decompose

D. 6.50 L

E. 65.0 L $13.0 \cancel{\text{L N}_2\text{O}_5} \times \frac{5 \text{ L gas (NO}_2 \text{ and O}_2\text{)}}{2 \cancel{\text{L N}_2\text{O}_5}} = 32.5 \text{ L}$

Ideal Gas Law

- With Combined Gas Law we saw that

$$\frac{PV}{T} = C$$

- With Avogadro's results we see that this is modified to

$$\frac{PV}{T} = nR$$

- Where R = a new constant = Universal Gas constant

$$PV = nRT$$

Ideal Gas Law

$$PV = nRT$$

- Equation of state of a gas
- If we know three of these variables, then we can calculate the fourth
- Can define *state* of the gas by defining three of these values

Ideal Gas

- Hypothetical gas that obeys ideal gas law relationship over all ranges of T , V , n and P
- As T increases and P decreases, real gases act as ideal gases

What is the value of R ?

- Plug in values of T , V , n and P for 1 mole of gas at STP (1 atm and 0.0 ° C)
 - $T = 0.0\text{ °C} = 273.15\text{ K}$
 - $P = 1\text{ atm}$
 - $V = 22.400\text{ L}$
 - $n = 1\text{ mol}$

$$R = \frac{PV}{nT} = \frac{1\text{ atm} \times 22.400\text{ L}}{1\text{ mol} \times 273.15\text{ K}}$$

$$R = 0.082057\text{ L atm mol}^{-1}\text{ K}^{-1}$$

Learning Check: $PV = nRT$

How many liters of $N_2(g)$ at 1.00 atm and 25.0 °C are produced by the decomposition of 150. g of NaN_3 ? $2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$

$$V = ?$$

$$P = 1 \text{ atm}$$

$$V = nRT/P$$

$$T = 25C + 273.15 = 298.15 \text{ K}$$

$$n = \text{mol } N_2 = \frac{150. \cancel{\text{g } NaN_3}}{1} \cdot \frac{1 \cancel{\text{mol } NaN_3}}{65.01 \cancel{\text{g}}} \cdot \frac{3 \text{ mol } N_2}{2 \cancel{\text{mol } NaN_3}}$$

$$n = 3.461 \text{ mol } N_2$$

$$V = \frac{(3.461 \cancel{\text{mol } N_2}) (0.082057 \frac{\cancel{\text{L} \cdot \text{atm}}}{\cancel{\text{mol} \cdot \text{K}}}) (298.15 \cancel{\text{K}})}{1.00 \cancel{\text{atm}}}$$

$$V = 84.6 \text{ L}$$

Example: Ideal Gas Law Problem^{10.5}

- What volume in milliliters does a sample of nitrogen with a mass of 0.245 g occupy at 21 ° C and 750 torr?
- What do I know?
 - Mass and identity (with the MM) of substance – can find moles
 - Temperature
 - Pressure
- What do I need to find?
 - Volume in mL

Example: Ideal Gas Law Problem ^{10.5}

Solution

$$V = ? \text{ (mL)}$$

$$\text{mass} = 0.245 \text{ g} \quad \text{MM} = 2 \times 14.0 = 28.0 \text{ g/mol}$$

- Convert temperature from ° C to K

$$T = 21^\circ \text{ C} + 273.15 \text{ K} = 294 \text{ K}$$

- Convert pressure from torr to atm

$$P = 750 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.987 \text{ atm}$$

- Convert mass to moles

$$n = \frac{m}{\text{MM}} = \frac{0.245 \text{ g}}{28.0 \text{ g mol}^{-1}} = 8.75 \times 10^{-3} \text{ mol}$$

Example: Ideal Gas Law Problem ^{10.5} Solution

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

$$V = \frac{(8.75 \times 10^{-3} \text{ moles})(0.082057 \text{ L atm mol}^{-1} \text{ K}^{-1})(294 \text{ K})}{0.987 \text{ atm}}$$

$$V = 0.214 \text{ L} \cdot \frac{1000 \text{ mL}}{1 \text{ L}} = 214 \text{ mL}$$

Your Turn!

Dry ice is solid carbon dioxide. What is the pressure, in atm, of CO_2 in a 50.0 L container at 35°C when 33.0 g of dry ice becomes a gas?

- A. 0.0432 atm
- B. 0.0101 atm
- C. 0.379 atm
- D. 0.0800 atm
- E. 37.9 atm

Your Turn! - Solution

$$\begin{aligned}
 \text{Pressure of CO}_2 &= \frac{\left(\cancel{33.0 \text{ g CO}_2} \right) \left(\frac{1 \cancel{\text{ mol CO}_2}}{44.01 \cancel{\text{ g CO}_2}} \right) (0.0821 \frac{\cancel{\text{ L atm}}}{\cancel{\text{ K mol}}}) (308 \cancel{\text{ K}})}{50.0 \cancel{\text{ L}}} \\
 &= 0.38 \text{ atm}
 \end{aligned}$$

Your Turn!

If 13.0 moles of N_2O_5 decompose into NO_2 and O_2 at 415 K in a 4.75 L container that can't expand or contract, after decomposition, how many times greater is the pressure in the box than atmospheric pressure (approx. 1 atm)?

- A. 13.0 times greater
- B. 32.5 times greater
- C. 466 times greater
- D. 93.2 times greater
- E. 233 times greater

Your Turn! solution



$$13.0 \cancel{\text{ mol N}_2\text{O}_5} \times \frac{5 \text{ mol gas (NO}_2 \text{ and O}_2\text{)}}{2 \cancel{\text{ mol N}_2\text{O}_5}} = 32.5 \text{ mol gas}$$

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

$$P = \frac{(\cancel{32.5 \text{ moles}})(0.082057 \cancel{\text{ L atm mol}^{-1} \text{ K}^{-1}})(\cancel{415 \text{ K}})}{4.75 \text{ L}}$$

$$P = 233 \text{ atm} \quad \frac{P_{\text{gas}}}{P_{\text{atm}}} = \frac{233 \cancel{\text{ atm}}}{1.00 \cancel{\text{ atm}}} = 233 \text{ times greater}$$

Determining Molecular Mass of Gas

If you know P , T , V and mass of gas

- Use ideal gas law to determine moles (n) of gas
- Then use mass and moles to get MM

If you know T , P , and density (d) of a gas

- Use density to calculate volume and mass of gas
- Use ideal gas law to determine moles (n) of gas
- Then use mass and moles to get MM

Example: Molecular Mass of a Gas^{10.5}

The label on a cylinder of an inert gas became illegible, so a student allowed some of the gas to flow into a 300. mL gas bulb until the pressure was 685 torr. The sample now weighed 1.45 g; its temperature was 27.0 ° C. What is the molecular mass of this gas? Which of the Group 7A gases (inert gases) was it?

- What do I know?
 - V , mass, T and P

Example: Molar Mass of a Gas

- $V = 300 \text{ mL} \cdot \frac{1 \text{ L}}{1000 \text{ mL}} = 0.300 \text{ L}$
- Mass = 1.45 g
- Convert T from $^{\circ} \text{C}$ to K
- $T = 27.0^{\circ} \text{C} + 273.15 \text{ K} = 300.2 \text{ K}$
- Convert P from torr to atm

$$P = 685 \text{ torr} \cdot \frac{1 \text{ atm}}{760 \text{ torr}} = 0.901 \text{ atm}$$

- Use V , P , and T to calculate n

$$n = \frac{PV}{RT} = \frac{(0.901 \text{ atm})(0.300 \text{ L})}{(0.082057 \text{ atm} \cdot \text{L} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(300.2 \text{ K})} = 0.01098 \text{ mole}$$

Example: Molar Mass of a Gas – Solution

- Now use the mass of the sample and the moles of the gas (n) to calculate the molar mass (MM)

$$\text{Molar Mass} = \frac{\text{mass}}{n} = \frac{1.45 \text{ g}}{0.01098 \text{ mol}} = \mathbf{132 \text{ g/mol}}$$

- Gas = Xe (Atomic Mass = 131.29 g/mol)

Example: Molecular Mass and Molecular Formula of a Gas

A gaseous compound of phosphorus and fluorine with an empirical formula of PF_2 was found to have a density of 5.60 g/L at 23.0°C and 750. torr. Calculate its molecular mass and its molecular formula.

- Know
 - Density
 - Temperature
 - Pressure

Example: Molecular Mass and Molecular Formula Solution

- $d = 5.60 \text{ g/L} \quad \therefore 1 \text{ L weighs } 5.60 \text{ g}$
- So assume you have 1 L of gas
- $V = 1.000 \text{ L}$
- Mass = 5.60 g
- Convert T from $^{\circ} \text{C}$ to K
- $T = 23.0^{\circ} \text{C} + 273.15 \text{ K} = 296.2 \text{ K}$
- Convert P from torr to atm

$$P = 750 \cancel{\text{ torr}} \cdot \frac{1 \text{ atm}}{760 \cancel{\text{ torr}}} = 0.9868 \text{ atm}$$

Example: Molecular Mass and Molecular Formula Solution

$$n = \frac{PV}{RT} = \frac{(0.9868 \text{ atm})(1.000 \text{ L})}{(0.082057 \text{ L atm mol}^{-1} \text{ K}^{-1})(296.2 \text{ K})} =$$

0.04058 mole

- Use n and mass to calculate molar mass

$$\text{Molar Mass} = \frac{\text{mass}}{n} = \frac{5.60 \text{ g}}{0.04058 \text{ mol}} = 138 \text{ g/mol}$$

Example: Molecular Mass and Molecular Formula Solution

- Now to find molecular formula given empirical formula and MM
- First find mass of empirical formula unit
- 1 P = 1 × 31 g/mol = 31 g/mol
- 2 F = 2 × 19 g/mol = 38 g/mol

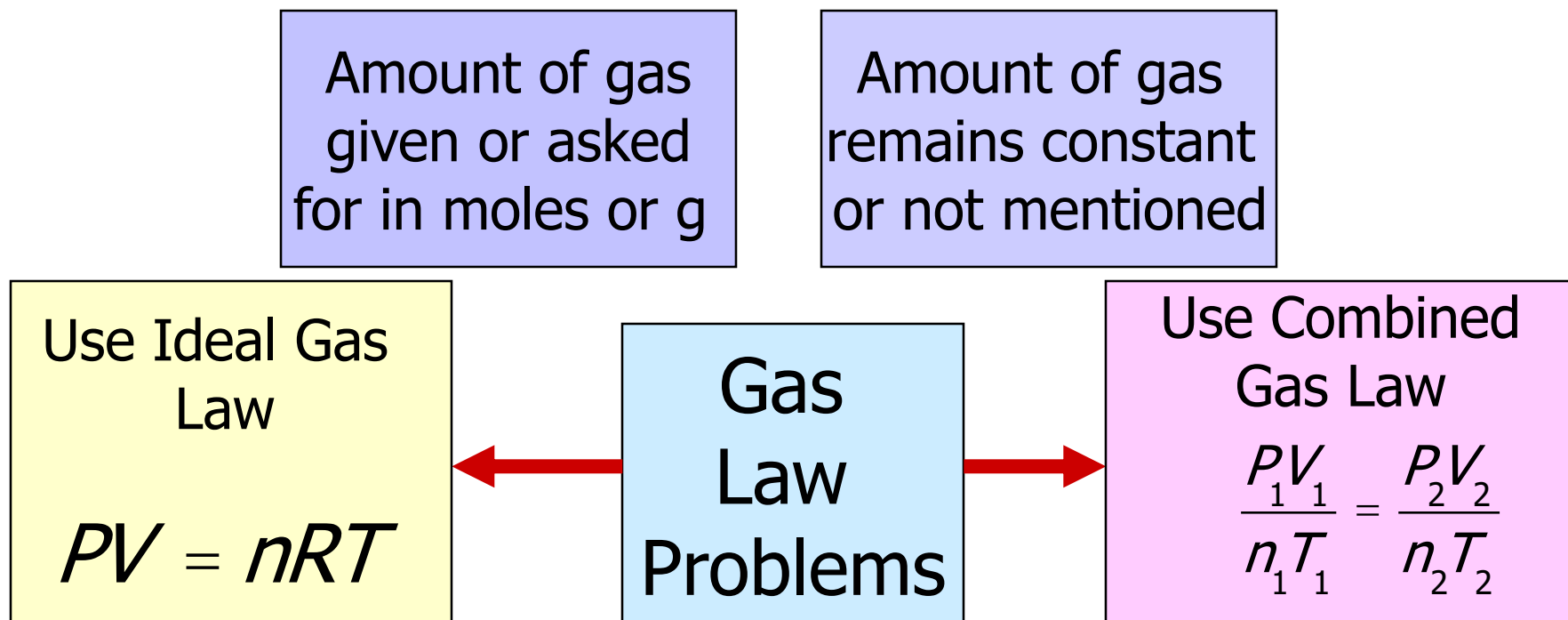
- Mass of PF₂ = 69 g/mol

$$\frac{\text{molecular mass}}{\text{empirical mass}} = \frac{138 \text{ g/mol}}{69 \text{ g/mol}} = 2$$

The correct molecular formula is P₂F₄

Which Gas Law to Use?

- **Which gas law to use in calculations?**
 - If you know ideal gas law, you can get all the rest



Your Turn!

A 7.52 g sample of a gas with an empirical formula of NO_2 occupies 2.00 L at a pressure of 1.00 atm and 25°C . Determine the molar mass and molecular formula of the compound.

- A. 45.0 g/mol, NO_2
- B. 90.0 g/mol, N_2O_4
- C. 7.72 g/mol, NO
- D. 0.0109 g/mol, N_2O
- E. Not enough data to determine molar mass

Your Turn! - Solution

$$\text{Molar Mass} = \frac{(7.52 \text{ g}) (0.0821 \cancel{\text{ L}} \cancel{\text{ atm}} \cancel{\text{ K}^{-1}} \text{ mol}^{-1}) (298 \cancel{\text{ K}})}{(1.0 \cancel{\text{ atm}}) (2.0 \cancel{\text{ L}})} = 90.0 \text{ g/mol}$$

$$\frac{90 \cancel{\text{ g mol}^{-1}}}{45.0 \cancel{\text{ g mol}^{-1}}} = 2$$

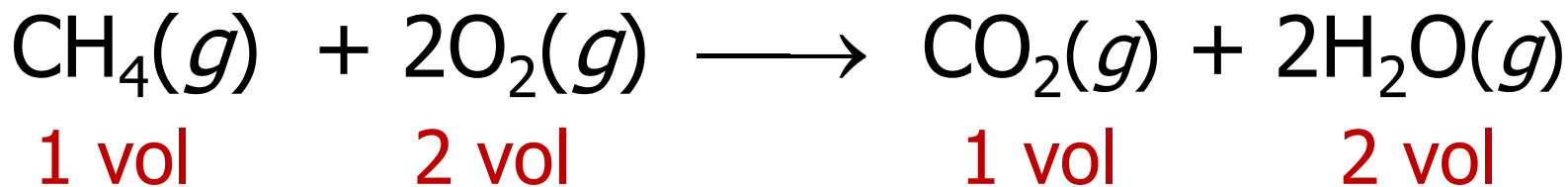
Molecular formula is N_2O_4

Stoichiometry of Reactions Between Gases

- Can use stoichiometric coefficients in equations to relate volumes of gases
 - Provided T and P are constant
 - Volume is proportional to moles ($V \propto n$)

Ex. Stoichiometry of Gases

Methane burns with the following equation:



- The combustion of 4.50 L of CH_4 consumes how many liters of O_2 ? (Both volumes measured at STP)
- P and T are all constant so just look at ratio of stoichiometric coefficients

$$\begin{aligned} \text{Volume of O}_2 &= 4.50 \cancel{\text{L}} \cdot \frac{2 \text{ L O}_2}{1 \cancel{\text{L CH}}_4} \\ &= 9.00 \text{ L O}_2 \end{aligned}$$

Ex. Stoichiometry of Gases

In one lab, the gas collecting apparatus used a gas bulb with a volume of 250. mL. How many grams of $\text{Na}_2\text{CO}_3(s)$ would be needed to prepare enough $\text{CO}_2(g)$ to fill this bulb when the pressure is at 738 torr and the temperature is 23°C ? The equation is:



Ex. Stoichiometry of Gases

- What do I know?
 - T , P , V and MM of Na_2CO_3
- What do I need to find?
 - Mass of Na_2CO_3
- How do I find this?
 - Use ideal gas law to calculate moles CO_2
 - Convert moles CO_2 to moles Na_2CO_3
 - Convert moles Na_2CO_3 to grams Na_2CO_3

Ex. Stoichiometry of Gases

1. Use ideal gas law to calculate moles CO₂

a. First convert mL to L

$$V = 250 \text{ mL} \cdot \frac{1 \text{ L}}{1000 \text{ mL}} = 0.250 \text{ L}$$

b. Convert torr to atm

$$P = 738 \text{ torr} \cdot \frac{1 \text{ atm}}{760 \text{ torr}} = 0.971 \text{ atm}$$

c. Convert °C to K

$$T = 23.0 \text{ °C} + 273.15 \text{ K} = 296.2 \text{ K}$$

Ex. Stoichiometry of Gases

1. Use ideal gas law to calculate moles CO₂

$$n = \frac{PV}{RT} = \frac{0.971 \text{ atm} \cdot 0.250 \text{ L}}{0.082057 \text{ atm L mol}^{-1} \text{ K}^{-1} \cdot 296.2 \text{ K}}$$

$$= 9.989 \times 10^{-3} \text{ mole CO}_2$$

2. Convert moles CO₂ to moles Na₂CO₃

$$9.989 \times 10^{-3} \text{ mol CO}_2 \cdot \frac{1 \text{ mol Na}_2\text{CO}_3}{1 \text{ mol CO}_2}$$

$$= 9.989 \times 10^{-3} \text{ mol Na}_2\text{CO}_3$$

Ex. Stoichiometry of Gases

3. Convert moles Na_2CO_3 to grams Na_2CO_3

$$9.989 \times 10^{-3} \text{ mol Na}_2\text{CO}_3 \times \frac{106 \text{ g Na}_2\text{CO}_3}{1 \text{ mol Na}_2\text{CO}_3} = 1.06 \text{ g Na}_2\text{CO}_3$$

Your Turn!



How many grams of sodium are required to produce 20.0 L of hydrogen gas at 25.0 ° C, and 750. torr?

- A. 18.6 g
- B. 57.0 g
- C. 61.3 g
- D. 9.62 g
- E. 37.1 g

Your Turn! - Solution

- Moles of H₂ produced

$$n = \frac{750 \text{ torr} \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) (20.0 \text{ L})}{(0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}) (298 \text{ K})} = 0.807 \text{ mol H}_2$$

- Grams of sodium required

$$\text{mass Na} = 0.807 \text{ mol H}_2 \left(\frac{2 \text{ mol Na}}{1 \text{ mol H}_2} \right) \left(\frac{23.0 \text{ g}}{1 \text{ mol Na}} \right) = 37.1 \text{ g}$$

Your Turn!

Solid sodium carbonate, when heated, decomposes to form sodium oxide and carbon dioxide. If 27.5 g of sodium carbonate is decomposed at 925 °C and the gas that results is collected in a 25.0 L container (assume $T_{\text{gas}} = 925 \text{ °C}$), would you worry about the container bursting?

- A. yes, high T will cause high P
- B. yes, P will be 102 atm (very high!)
- C. no, P will only be 1.02 atm
- D. no, P will only be 0.788 atm

Your Turn! – Solution



$$27.5 \text{ g } \cancel{\text{Na}_2\text{CO}_3} \times \left(\frac{\cancel{1 \text{ mol Na}_2\text{CO}_3}}{\cancel{106 \text{ g Na}_2\text{CO}_3}} \right) \times \left(\frac{1 \text{ mol CO}_2}{\cancel{1 \text{ mol Na}_2\text{CO}_3}} \right)$$

$$= 0.259 \text{ mol CO}_2$$

$$P = \frac{(\cancel{0.259 \text{ moles}})(\cancel{0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}})(\cancel{1198 \text{ K}})}{25.0 \text{ L}}$$

$$P = 1.02 \text{ atm}$$

This is close to regular atmospheric pressure, so no concern about bursting

Dalton's Law of Partial Pressure

- For mixture of non-reacting gases in container
- Total pressure exerted is sum of the individual partial pressures that each gas would exert alone
- $P_{\text{total}} = P_a + P_b + P_c + \dots$
- Where P_a , P_b , and P_c are the partial pressures
- Partial pressure
 - Pressure that particular gas would exert if it were alone in container

Dalton's Law of Partial Pressures

- Assuming each gas behaves ideally
- Partial pressure of each gas can be calculated from ideal gas law

$$P_a = \frac{n_a RT}{V} \quad P_b = \frac{n_b RT}{V} \quad P_c = \frac{n_c RT}{V}$$

- So total pressure is

$$\begin{aligned} P_{\text{total}} &= P_a + P_b + P_c + \dots \\ &= \frac{n_a RT}{V} + \frac{n_b RT}{V} + \frac{n_c RT}{V} + \dots \end{aligned}$$

Dalton's Law of Partial Pressures

- Rearranging

$$P_{\text{total}} = (n_a + n_b + n_c + \dots) \frac{RT}{V}$$

- Or

$$P_{\text{total}} = n_{\text{total}} \frac{RT}{V}$$

- Where $n_{\text{total}} = n_a + n_b + n_c + \dots$

n_{total} = sum of number moles of various gases in mixture

Dalton's Law of Partial Pressures^{10.6}

Means for mixture of ideal gases

- Total number of moles of particles is important
 - Not composition or identity of involved particles
- Pressure exerted by ideal gas not affected by identity of gas particles
- Reveals two important facts about ideal gases
 1. Volume of individual gas particles must be important
 2. Forces among particles must not be important
 - If they were important, P would be dependent on identity of gas

Example: Partial Pressure

Mixtures of helium and oxygen are used in scuba diving tanks to help prevent “the bends.” For a particular dive, 46 L He at 25 ° C and 1.0 atm and 12 L O₂ at 25 ° C and 1.0 atm were pumped into a tank with a volume of 5.0 L. Calculate the partial pressure of each gas and the total pressure in the tank at 25 ° C.

Example: Partial Pressure – Solution

- Have two sets of conditions
 - Before and after being put into the tank

He			O ₂	
$P_i = 1.0 \text{ atm}$	$P_f = P_{\text{He}}$		$P_i = 1.0 \text{ atm}$	$P_f = P_{\text{O}_2}$
$V_i = 46 \text{ L}$	$V_f = 5.0 \text{ L}$		$V_i = 12 \text{ L}$	$V_f = 5.0 \text{ L}$

Example: Partial Pressure – Solution

- First calculate pressure of each gas in 5 L tank (P_f) using combined gas law

$$P_{He} = \frac{P_i V_i}{V_f} = \frac{1.0 \text{ atm} \times 46 \cancel{\text{ L}}}{5.0 \cancel{\text{ L}}} = 9.2 \text{ atm}$$

$$P_{O_2} = \frac{P_i V_i}{V_f} = \frac{1.0 \text{ atm} \times 12 \cancel{\text{ L}}}{5.0 \cancel{\text{ L}}} = 2.4 \text{ atm}$$

- Then use these partial pressures to calculate total pressure

$$P_{\text{total}} = P_{He} + P_{O_2} = 9.2 \text{ atm} + 2.4 \text{ atm} = 11.6 \text{ atm}$$

Your Turn!

A mixture of 250 mL of methane, CH_4 , at 35°C and 0.55 atm and 750 mL of propane, C_3H_8 , at 35°C and 1.5 atm, were introduced into a 10.0 L container. What is the final pressure, in torr, of the mixture?

- A. 95.6 torr
- B. 6.20×10^4 torr
- C. 3.4×10^3 torr
- D. 760 torr
- E. 60 torr

Your Turn! - Solution

$$P_{\text{CH}_4} = \frac{(0.55 \text{ atm})(0.250 \cancel{\text{ L}})}{10.0 \cancel{\text{ L}}} = 0.0138 \text{ atm}$$

$$P_{\text{C}_3\text{H}_8} = \frac{(1.5 \text{ atm})(0.750 \cancel{\text{ L}})}{10.0 \cancel{\text{ L}}} = 0.112 \text{ atm}$$

$$P_{\text{T}} = (0.0138 \text{ atm} + 0.112 \text{ atm}) \left(\frac{760 \text{ torr}}{1 \text{ atm}} \right) = 95.6 \text{ torr}$$

Mole Fractions and Mole Percents ^{10.6}

Mole Fraction (x)

- Ratio of number moles of given component in mixture to total number moles in mixture

$$C_A = \frac{n_A}{n_A + n_B + n_C + \dots + n_Z} = \frac{n_A}{n_{\text{total}}}$$

Mole Percent (mol %)

$$\text{Mole \%} = C_A \cdot 100\%$$

Your Turn!

A mixture consists of 122 blue, 137 red, and 212 yellow M&Ms. What is the fraction of each?

- A. 0.259 blue, 0.291 red, 0.450 yellow
- B. 0.803 blue, 0.206 red, 0.320 yellow
- C. 0.122 blue, 0.137 red, 0.212 yellow
- D. 3.86 blue, 3.44 red, 2.22 yellow
- E. 1.75 blue, 1.46 red, 4.53 yellow

$$\text{for blue : } \frac{122 \text{ blue}}{122 + 137 + 212 \text{ total}} = 0.259$$

Your Turn!

A mixture consists of 122 moles of N_2 , 137 moles of C_3H_8 , and 212 moles of CO_2 . What is the mole fraction of each?

A. 0.259 N_2 , 0.291 C_3H_8 , 0.450 CO_2

B. 0.803 N_2 , 0.206 C_3H_8 , 0.320 CO_2

C. 0.122 N_2 , 0.137 C_3H_8 , 0.212 CO_2

D. 3.86 N_2 , 3.44 C_3H_8 , 2.22 CO_2

E. 1.75 N_2 , 1.46 C_3H_8 , 4.53 CO_2

$$\text{for } \text{N}_2 : \frac{122 \text{ moles } \text{N}_2}{122 + 137 + 212 \text{ total}} = 0.259$$

Mole Fractions of Gases from Partial Pressures

$$n_A = P_A \left(\frac{V}{RT} \right)$$

- If V and T are constant then, $\frac{V}{RT} = \text{constant}$
- For mixture of gases in one container

$$X_A = \frac{P_A \left(\frac{V}{RT} \right)}{P_A \left(\frac{V}{RT} \right) + P_B \left(\frac{V}{RT} \right) + P_C \left(\frac{V}{RT} \right) + \dots + P_Z \left(\frac{V}{RT} \right)}$$

Mole Fractions of Gases from Partial Pressures

$\frac{V}{RT}$ cancels, leaving

$$C_A = \frac{P_A}{P_A + P_B + P_C + \text{xxxx} + P_Z}$$

or

$$C_A = \frac{P_A}{P_{\text{total}}} = \frac{n_A}{n_{\text{total}}}$$

Example: Partial Pressures

- The partial pressure of oxygen was observed to be 156 torr in air with a total atmospheric pressure of 743 torr. Calculate the mole fraction of O₂ present

- Use
$$C_A = \frac{P_A}{P_{\text{total}}}$$

$$C_{\text{O}_2} = \frac{156 \text{ torr}}{743 \text{ torr}} = 0.210$$

Partial Pressures and Mole Fractions

- Partial pressure of particular component of gaseous mixture
- Equals mole fraction of that component times total pressure

$$P_A = C_A \cdot P_{total}$$

Example: Partial Pressure

The mole fraction of nitrogen in the air is 0.7808. Calculate the partial pressure of N₂ in air when the atmospheric pressure is 760. torr.

$$P_{\text{N}_2} = C_{\text{N}_2} \cdot P_{\text{total}}$$

$$P_{\text{N}_2} = 0.7808 \cdot 760 \text{ torr} = 593 \text{ torr}$$

Your Turn!

A mixture of 250 mL of methane, CH_4 , at 35°C and 0.55 atm and 750 mL of propane, C_3H_8 , at 35°C and 1.5 atm was introduced into a 10.0 L container. What is the mole fraction of methane in the mixture?

- A. 0.50
- B. 0.11
- C. 0.89
- D. 0.25
- E. 0.33

Your Turn! - Solution

$$P_{\text{CH}_4} = \frac{0.55 \text{ atm} \cdot 0.250 \cancel{\text{ L}}}{10.0 \cancel{\text{ L}}} = 0.0138 \text{ atm}$$

$$P_{\text{C}_3\text{H}_8} = \frac{1.5 \text{ atm} \cdot 0.750 \cancel{\text{ L}}}{10.0 \cancel{\text{ L}}} = 0.112 \text{ atm}$$

$$C_{\text{CH}_4} = \frac{0.0138 \cancel{\text{ atm}}}{0.0138 \cancel{\text{ atm}} + 0.112 \cancel{\text{ atm}}} = 0.110$$

Answer is ultimately limited to two significant figures by the numerator which rigorously is only allowed two significant figures

Your Turn!

A mixture consists of 122 moles of N_2 , 137 moles of C_3H_8 , and 212 moles of CO_2 at 200 K in a 75.0 L container. What is the total pressure of the gas and the partial pressure of CO_2 ?

- A. 46.4 atm, 20.9 atm
- B. 103 atm, 26.7 atm
- C. 103 atm, 46.4 atm
- D. 103 atm, 29.9 atm
- E. 46.4 atm, 46.4 atm

Your Turn! – Solution

$$P_{\text{total}} = \frac{(\cancel{471 \text{ moles}})(\cancel{0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}})(\cancel{200 \text{ K}})}{75.0 \cancel{\text{ L}}}$$

$$P_{\text{total}} = 103 \text{ atm}$$

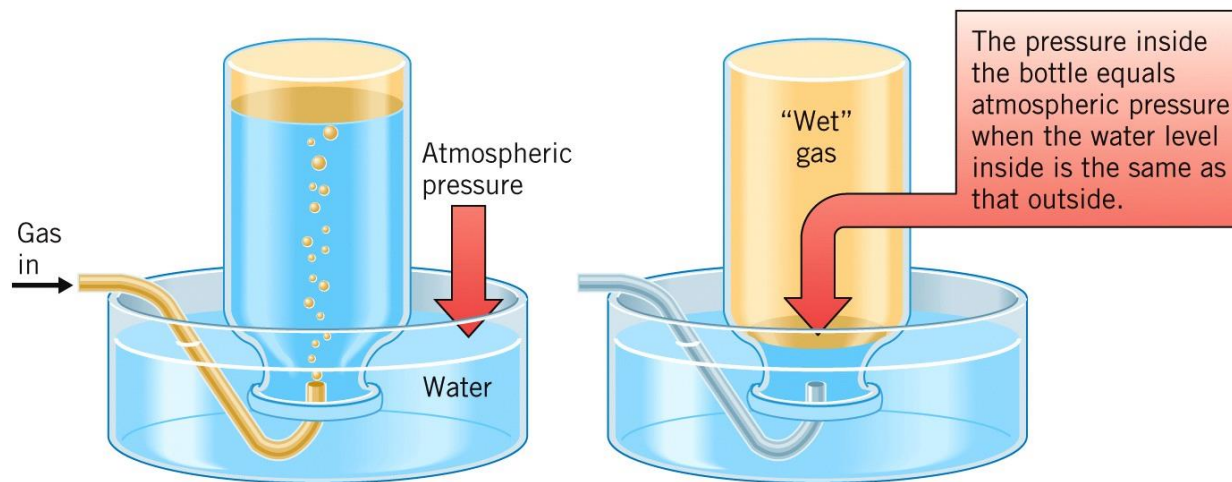
$$\text{mole fraction CO}_2 : \frac{212 \text{ moles CO}_2}{122 + 137 + 212 \text{ total}} = 0.450$$

$$P_{\text{CO}_2} = (\chi_{\text{CO}_2})(P_{\text{total}}) = (0.450)(103 \text{ atm})$$

$$P_{\text{CO}_2} = 46.4 \text{ atm}$$

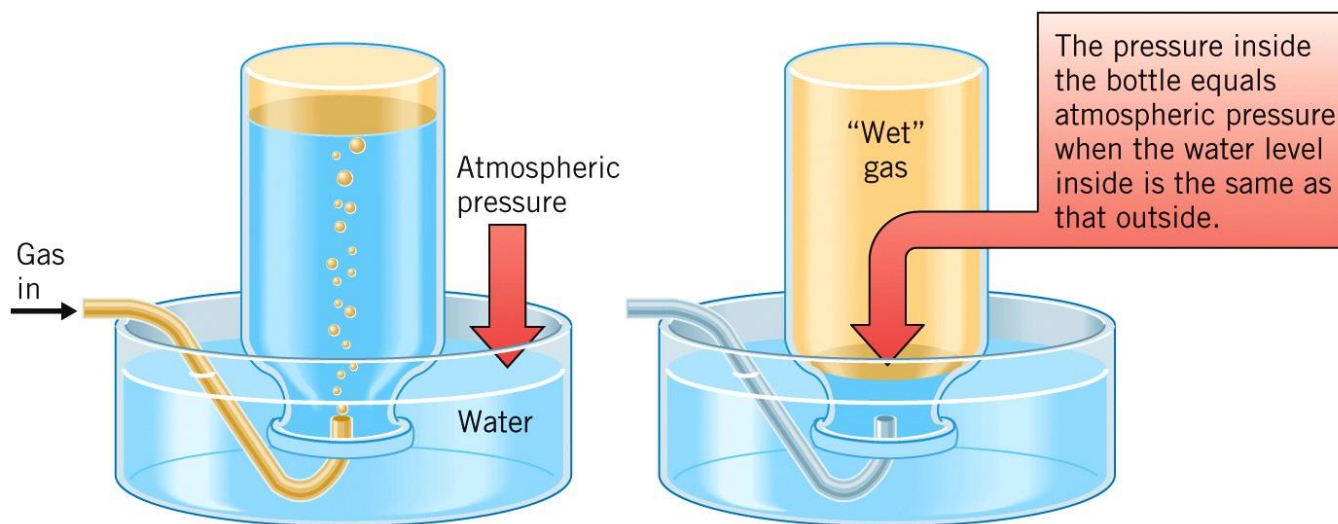
Collecting Gases over Water

- Application of Dalton's Law of Partial Pressures
- Gases that don't react with water can be trapped over water
- Whenever gas is collected by displacement of water, mixture of gases results
 - Gas in bottle is mixture of water vapor and gas being collected



Collecting Gases over Water

- Water vapor is present because molecules of water escape from surface of liquid and collect in space above liquid
- Molecules of water return to liquid
- When rate of escape = rate of return
 - Number of water molecules in vapor state remains constant
- Gas saturated with water vapor = “Wet” gas



Vapor Pressure

- Pressure exerted by vapor present in space above any liquid
 - Constant at constant T
- When wet gas collected over water, we usually want to know how much “dry” gas this corresponds to
 - $P_{total} = P_{gas} + P_{water}$
- Rearranging
 - $P_{gas} = P_{total} - P_{water}$

Example: Collecting Gas over Water

A sample of oxygen is collected over water at 20.0 °C and a pressure of 738 torr. Its volume is 310 mL. The vapor pressure of water at 20 °C is 17.54 torr.

- What is the partial pressure of O₂?
- What would the volume be when dry at STP?

a.
$$P_{O_2} = P_{total} - P_{water}$$
$$= 738 \text{ torr} - 17.5 \text{ torr} = 720 \text{ torr}$$

Ex. Collecting Gas – (Soln.)

b. Use the combined gas law to calculate P_{O_2} at STP

$$P_1 = 720 \text{ torr} \quad P_2 = 760 \text{ torr}$$

$$V_1 = 310 \text{ mL} \quad V_2 = ?$$

$$T_1 = 20.0 + 273.15 = 293 \text{ K}$$

$$T_2 = 0.0 + 273 \text{ K} = 273 \text{ K}$$

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

$$V_2 = \frac{(\cancel{720 \text{ torr}})(310 \text{ mL})(\cancel{273 \text{ K}})}{(\cancel{293 \text{ K}})(\cancel{760 \text{ torr}})}$$

$$V_2 = 274 \text{ mL}$$

Your Turn!

An unknown gas was collected by water displacement. The following data was recorded:

$$T = 27.0 \text{ }^\circ\text{C}; \quad P = 750 \text{ torr};$$

$$V = 37.5 \text{ mL}; \quad \text{Gas mass} = 0.0873 \text{ g};$$

$$P_{\text{H}_2\text{O}(\text{vap})} = 26.98 \text{ torr}$$

Determine the molecular weight of the gas.

A. 5.42 g/mol

B. 30.2 g/mol

C. 60.3 g/mol

D. 58.1 g/mol

E. 5.81 g/mol

Your Turn! - Solution

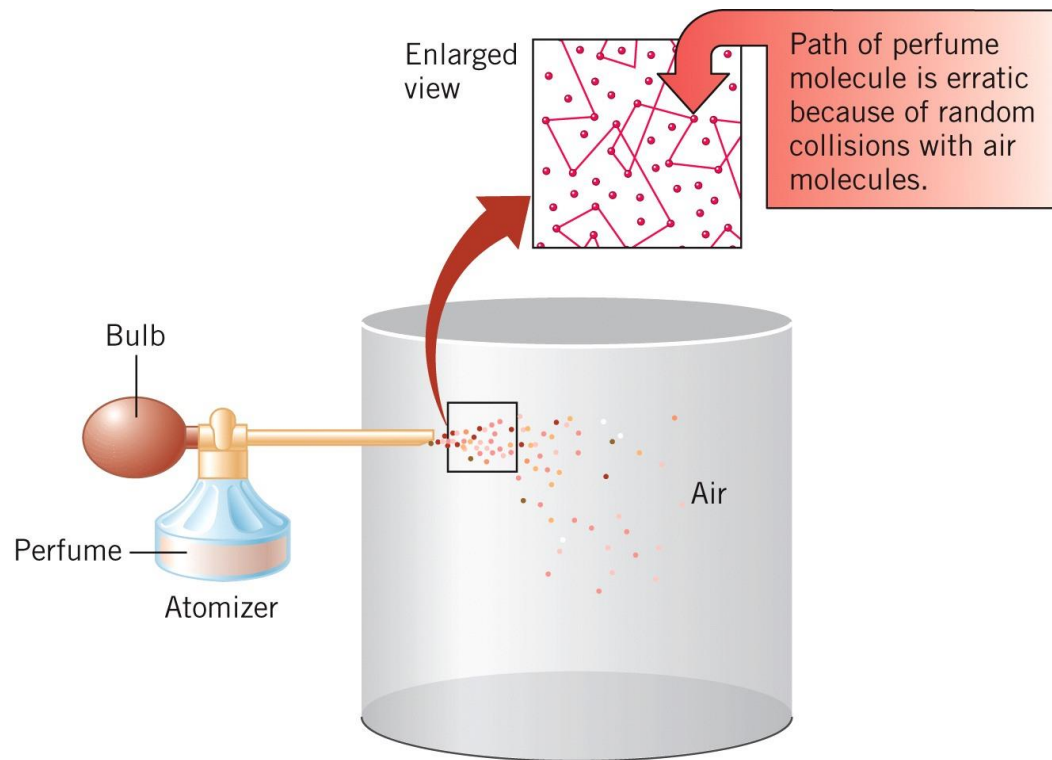
$$\text{Molar Mass} = \frac{gRT}{PV} = \frac{(0.0873 \text{ g}) (0.0821 \cancel{\text{ L}} \cancel{\text{ atm}} \cancel{\text{ K}^{-1}} \text{ mol}^{-1}) (300 \cancel{\text{ K}})}{(750 \cancel{\text{ torr}} - 26.98 \cancel{\text{ torr}}) (0.0375 \cancel{\text{ L}})} \left(\frac{760 \cancel{\text{ torr}}}{1 \cancel{\text{ atm}}} \right)$$

$$= 60.3 \text{ g/mol}$$

Diffusion

- Complete spreading out and intermingling of molecules of one gas into and among those of another gas

- e.g.**, Perfume in room (if convective forces are absent)

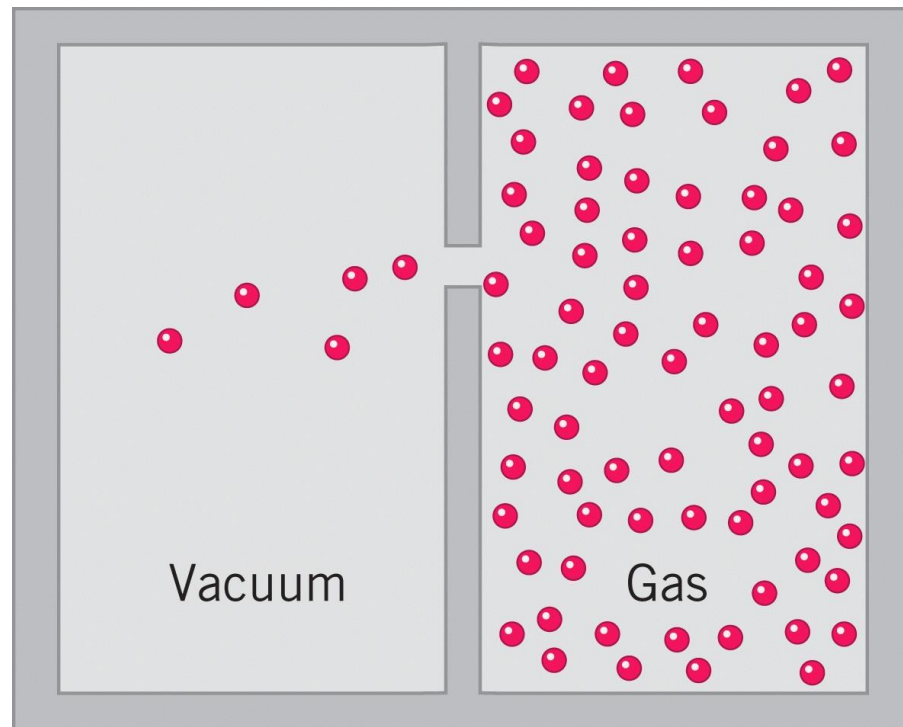


Effusion

- Movement of gas molecules
- Through extremely small opening into vacuum

Vacuum

- No other gases present in other half



Thomas Graham

- Studied relationship between effusion rates and molecular masses for series of gases
- Wanted to minimize collisions
 - Slow molecules down
 - Make molecules bump aside or move to rear

Graham's Law of Effusion

- Rates of effusion of gases are inversely proportional to square roots of their densities, d , when compared at identical pressures and temperatures

$$\text{Effusion Rate} \propto \frac{1}{\sqrt{d}} \quad (\text{constant } P \text{ and } T)$$

$$\text{Effusion Rate} \times \sqrt{d} = k \quad (\text{constant } P \text{ and } T)$$

k is virtually identical for all gases

$$\text{Effusion Rate (A)} \times \sqrt{d_A} = \text{Effusion Rate (B)} \times \sqrt{d_B} = k$$

Graham's Law of Effusion

- Rearranging

$$\frac{\text{Effusion Rate (A)}}{\text{Effusion Rate (B)}} = \frac{\sqrt{d_B}}{\sqrt{d_A}} = \sqrt{\frac{d_B}{d_A}}$$

- Finally, $d_A \propto MM$ (constant V and n)

$$\frac{\text{Effusion Rate (A)}}{\text{Effusion Rate (B)}} = \sqrt{\frac{d_B}{d_A}} = \sqrt{\frac{M_B}{M_A}}$$

- Result: Rate of effusion is inversely proportional to molecular mass of gas

$$\text{Effusion Rate} \times \sqrt{MM} = k \quad (\text{constant } P \text{ and } T)$$

Graham's Law of Effusion

$$\text{Effusion Rate} \times \sqrt{MM} = k$$

- Heavier gases effuse more slowly
- Lighter gases effuse more rapidly

Graham's Law of Effusion

Example: Calculate the ratio of the effusion rates of hydrogen gas (H_2) and uranium hexafluoride (UF_6) - a gas used in the enrichment process to produce fuel for nuclear reactors.

Recall

$$\text{Effusion Rate} \times \sqrt{MM} = k$$

Example: Effusion

- First must compute MM 's
 - $MM(\text{H}_2) = 2.016 \text{ g/mol}$
 - $MM(\text{UF}_6) = 352.02 \text{ g/mol}$

$$\frac{\text{Effusion Rate}(\text{H}_2)}{\text{Effusion Rate}(\text{UF}_6)} = \sqrt{\frac{M_{\text{UF}_6}}{M_{\text{H}_2}}} = \sqrt{\frac{352.02}{2.016}} = 13.21$$

- Thus the very light H_2 molecules effuse ~ 13 times as fast as the massive UF_6 molecules.

Your Turn!

If it takes methane 3.0 minutes to diffuse 10.0 m, how long will it take sulfur dioxide to travel the same distance?

- A. 1.5 min
- B. 12.0 min
- C. 1.3 min
- D. 0.75 min
- E. 6.0 min

Your Turn! - Solution

Remember, velocity and time are inversely related.

$$\frac{t_1}{t_2} = \sqrt{\frac{MW_1}{MW_2}}$$

$$\frac{3.0 \text{ min}}{t_2} = \sqrt{\frac{16.04 \text{ g/mol}}{64.06 \text{ g/mol}}}$$

$$t_2 = 6.0 \text{ min}$$

Example: Effusion

- For the series of gases He, Ne, Ar, H₂, and O₂ what is the order of increasing rate of effusion?

Substance	He	Ne	Ar	H ₂	O ₂
MM	4	20	40	2	32

- Lightest are fastest
- So H₂ > He > Ne > O₂ > Ar

Your Turn!

How many times faster does $^{235}\text{UF}_6$ (MW = 349.0 g/mol) effuse compared to $^{238}\text{UF}_6$ (MW = 352.0 g/mol)?

A. 0.9957

B. 1.004

C. 0.994

D. 1.009

E. 0.9911

$$\frac{\text{Rate (235)}}{\text{Rate (238)}} = \sqrt{\frac{M_{^{238}\text{UF}_6}}{M_{^{235}\text{UF}_6}}} = \sqrt{\frac{352.0 \text{ g/mol}}{349.0 \text{ g/mol}}} = 1.004$$

$$\text{Rate (235)} = 1.004 \times \text{Rate (238)}$$

Kinetic Theory and Gas Laws

- So far, considered gases from experimental point of view
 - At $P < 1$ atm, most gases approach ideal
- Ideal gas law predicts behavior
 - Does not explain it
- Recall scientific method
 - Law is generalization of many observations
 - Laws allow us to predict behavior
 - Do not explain why

Kinetic Theory and the Gas Law^{10.7}

- To answer WHY it happens—must construct theory or model
 - Models consist of speculations about what individual atoms or molecules might be doing to cause observed behavior of macroscopic system (large number of atoms/molecules)
- For model to be successful
 - Must explain observed behavior in question
 - Predict correctly results of future experiments

Kinetic Theory and the Gas Law^{10.7}

- Theories can never be proved absolutely true
 - Often valid within defined boundaries
 - Approximation by its very nature
 - Bound to fail at some point
- One example is kinetic theory of gases
 - Attempts to explain properties of ideal gases.
 - Describes behavior of individual gas particles

Postulates of Kinetic Theory of Gases

1. Particles are so small compared with distances between them that the volume of individual particles is negligible.

- $V_{\text{gas}} \sim 0$

2. Particles are in constant motion

- Collisions of particles with walls of container are cause of pressure exerted by gas

- Number collisions $\propto P_{\text{gas}}$

Postulates of Kinetic Theory of Gases

3. Particles exert no force on each other
 - They neither attract nor repel each other
4. Average kinetic energy of collection of gas particles is directly proportional to Kelvin temperature
 - $KE_{\text{avg}} \propto T_{\text{K}}$

Kinetic Theory of Gases

- Kinetic theory of matter and heat transfer (Chapter 7)
- Heat $\propto PV \propto KE_{\text{ave}}$
- But for constant number of moles of ideal gas
- $PV = nRT$
 - Where nR is proportionality constant
- This means $T \propto KE_{\text{ave}}$
- Specifically
$$KE_{\text{ave}} = \frac{3}{2}RT$$
- As T increases, KE_{ave} increases
 - Increase in number collisions with walls, thereby increasing pressure

Real Gases

- Don't conform to these assumptions
- Have finite volumes
- Do exert forces on each other
- However, kinetic theory of gases does explain ideal gas behavior
- True test of model is how well its predictions fit experimental observations

Postulates of Kinetic Theory of Gases^{10.7}

- Picture ideal gas consisting of particles having no volume and no attractions for each other
- Assumes that gas produces pressure on its container by collisions with walls

Kinetic Theory Explains Gas Laws

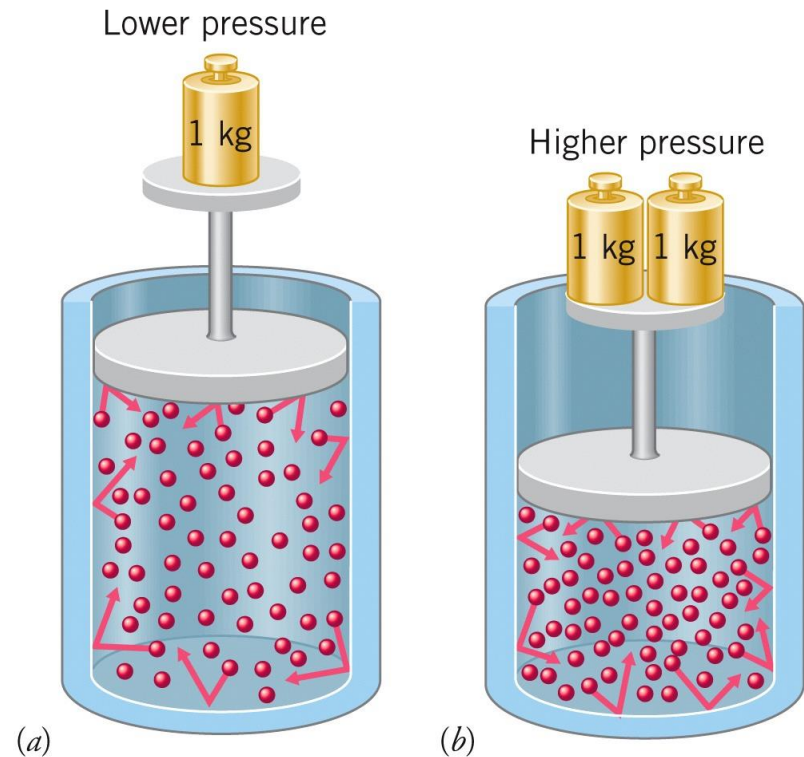
P and V (Boyle's Law)

- For given sample of ideal gas at given T (n and T constant)
- If V decreases, P increases

$$P = (nRT) \frac{1}{V}$$

By kinetic theory of gases

- Decrease in V , means gas particles hit wall more often
- Increase P



***P* and *T* (Gay-Lussac's Law)**

- For given sample of ideal gas at constant V (n and V constant)
- P is directly proportional to T

$$P = \frac{nR}{V} T$$

***P* and *T* (Gay-Lussac's Law)**

Kinetic theory of gases accounts for this

- As T increases
- KE_{ave} increases
- Speeds of molecules increases
- Gas particles hit wall more often as V same
- So P increases

T and V (Charles' Law)

- For given sample of ideal gas at constant P
(n and P constant)
- V is directly proportional to T

$$V = \frac{nR}{P} T$$

T and V (Charles' Law)

Kinetic theory of gases accounts for this

- As T increases
- KE_{ave} increases
- Speeds of molecules increases
- Gas particles hit wall more often as pressure remains the same
- So volume increases

V and n (Avogadro's Principle)

- For ideal gas at constant T and P
- V is directly proportional to n

$$V = \frac{RT}{P} n$$

- Kinetic Theory of Gases account for this
 - As the number of moles of gas particles increase at same T
 - Holding T and P constant
 - Must V must increase

Dalton's Theory of Partial Pressures^{10.7}

$$P_{total} = \sum P_{\text{individual gases}}$$

- Expected from kinetic theory of gases
 - All gas particles are independent of each other
 - Volume of individual particles is unimportant
 - Identities of gases do not matter
- Conversely, can think of Dalton's Law of Partial Pressures as evidence for kinetic theory of gases
 - Gas particles move in straight lines, neither attracting nor repelling each other
 - Particles act independently
 - Only way for Dalton's Law to be valid

Law of Effusion (Graham's Law)

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

- Key conditions:
 - Comparing two gases at same P and T
 - Conditions where gases don't hinder each other
 - Hence, particles of two gases have same KE_{ave}

$$\overline{\text{KE}}_1 = \overline{\text{KE}}_2$$
 - Let $\overline{v^2}$ = average of velocity squared of molecules of gases
 - Then
$$\frac{1}{2} m_1 \overline{v_1^2} = \frac{1}{2} m_2 \overline{v_2^2}$$

Law of Effusion (Graham's Law)

- Rearranging $\frac{\overline{v_1^2}}{\overline{v_2^2}} = \frac{m_1}{m_2}$

- Taking square root of both sides

$$\frac{\overline{v_1}}{\overline{v_2}} = \sqrt{\frac{m_1}{m_2}}$$

- Since $m_1 \propto M_1$ $\frac{\overline{v_1}}{\overline{v_2}} = \sqrt{\frac{m_1}{m_2}} = \sqrt{\frac{M_1}{M_2}}$

- Now Rate of effusion $\propto \overline{v}$

- So Effusion rate = $k \overline{v}$

$$\frac{\text{Effusion rate of gas}_1}{\text{Effusion rate of gas}_2} = \sqrt{\frac{M_2}{M_1}}$$

Absolute Zero

$$T \propto KE_{ave} \propto \frac{1}{2} m(\overline{v^2})$$

- If $KE_{ave} = 0$, then T must = 0.
- Only way for $KE_{ave} = 0$, is if $v = 0$ since $m \neq 0$.
- When gas molecules stop moving, then gas as cold as it can get
- Absolute zero

Real Gases: Deviations from Ideal Gas Law^{10.7}

- Combined Gas Law $\frac{PV}{T} = \text{constant}$
- Ideal Gas Law $\frac{PV}{nT} = R$
- Real gases deviate Why?