

Chapter 11

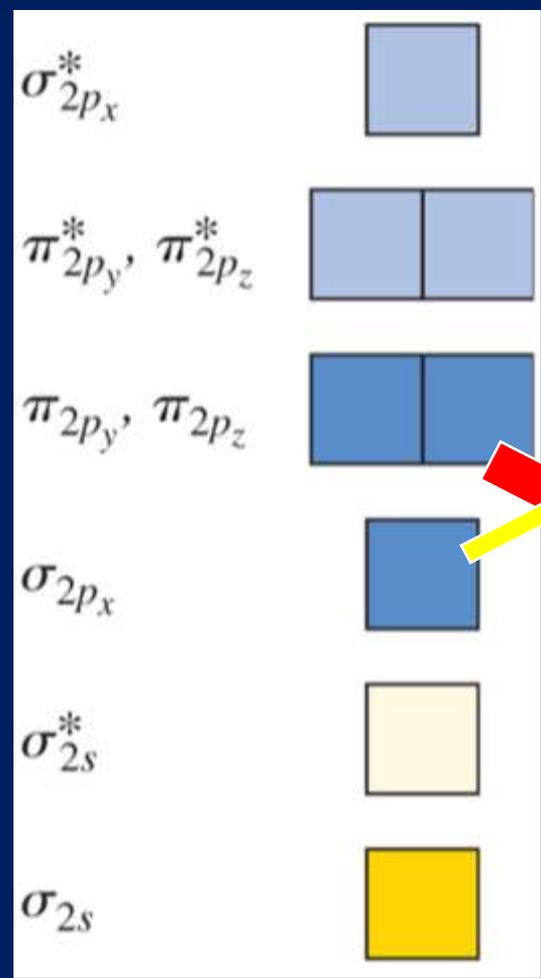
Gases

Energy order of the π_{2p} and σ_{2p} orbitals changes across the period.

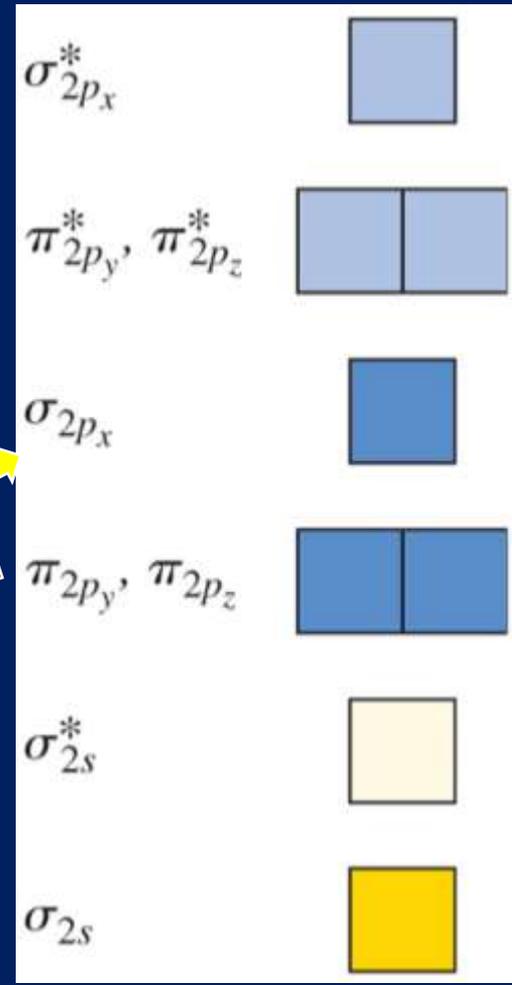
Due to lower nuclear charge of B, C & N there is no s-p orbitals interaction

Due to high nuclear charge of O, F & Ne there is an s-p orbitals interaction

This is the correct order of molecular orbitals. The order given in the same slide of the presentation on Chapter 9 is wrong.



O_2, F_2, Ne_2



B_2, C_2, N_2

Topics

- **Properties of gases**
- **The gas laws Avogadro**
- **The ideal gas equation**
- **Reactions with gaseous reactants and products**
- **Gas mixtures**
- **The kinetic molecular theory of gases**
- **Deviation from ideal behavior**

11.1 Properties of Gases

- The properties of a gas are almost independent of its identity.

(Gas molecules behave as if no other molecules are present.)

- Compressible (gas molecules are far apart from each other)
- Low density compared to liquids and solids
- Expand to fill a container (assume the shape and the volume of its container)
- Form homogeneous mixtures with one another in any proportion.

Gas pressure: definition

- **Pressure:** force per unit area

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

- **newton (N):** Unit of force

$$1 \text{ N} = 1 \text{ kg} \cdot \text{m/s}^2$$

- **pascal (Pa):** Unit of pressure

$$1 \text{ Pa} = 1 \text{ N/m}^2$$

- **Standard pressure**

1 atm*

101,325 Pa

760 mmHg*

760 torr*

1.01325 bar

14.7 psi

*These are exact numbers.

Gas pressure: units

TABLE 11.2

Units of Pressure Commonly Used in Chemistry

Unit	Origin	Definition
standard atmosphere (atm)	Pressure at sea level	1 atm = 101,325 Pa
mmHg	Barometer measurement	1 mmHg = 133.322 Pa
torr	Name given to mmHg in honor of Torricelli, the inventor of the barometer	1 torr = 133.322 Pa
bar	Same order of magnitude as atm, but a decimal multiple of Pa	1 bar = 1×10^5 Pa

Standard Atmospheric Pressure:

1 atm = 76 cm Hg = 760 mm Hg = 760 Torr = 101,325 Pa

Very small unit, thus it is not commonly used

If a weatherman says that atmospheric pressure is 29.12 inches of mercury, what is it in torr?

$$29.12 \text{ in} \left(\frac{2.54 \text{ cm}}{1 \text{ in}} \right) \left(\frac{10 \text{ mm}}{1 \text{ cm}} \right) \left(\frac{1 \text{ torr}}{1 \text{ mm}} \right) = 739.6 \text{ torr}$$

Example

A. What is 475 mm Hg expressed in atm?

$$475 \text{ mm Hg} \times \frac{1 \text{ atm}}{760 \text{ mm Hg}} = 0.625 \text{ atm}$$

B. The pressure of a tire is measured as 29.4 psi.

What is this pressure in mm Hg?

$$29.4 \text{ psi} \times \frac{1.00 \text{ atm}}{14.7 \text{ psi}} \times \frac{760 \text{ mmHg}}{1.00 \text{ atm}} = 1.52 \times 10^3 \text{ mmHg}$$

- **Calculation of atmospheric pressure**

Area
1 cm x 1 cm
or
0.0001 m²



Mass: 1 kg

$$1 \text{ kg} \times \frac{9.80665 \text{ m}}{\text{s}^2} \approx 10 \text{ kg} \cdot \text{m/s}^2 = 10 \text{ N}$$

where 9.80665 m/s² is the gravitational constant.

$$\frac{10 \text{ N}}{0.0001 \text{ m}^2} = 1 \times 10^5 \text{ Pa}$$

Measurement of pressure Torricellian Barometer



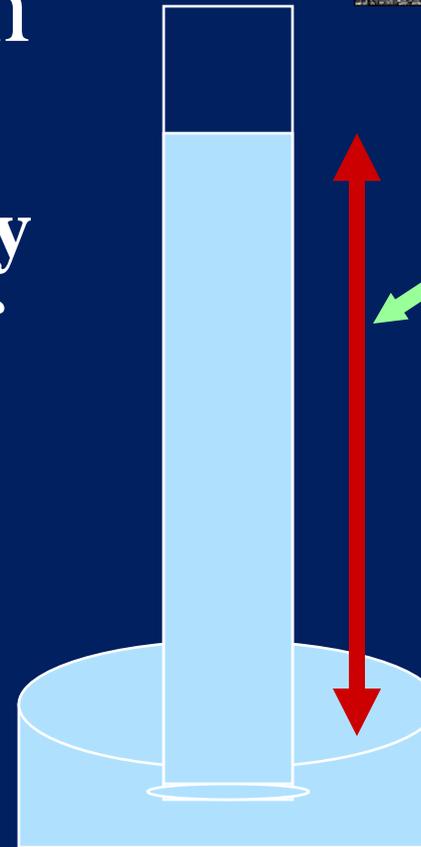
Barometer: an instrument used to measure atmospheric pressure

760 mmHg

$$P = d \cdot g \cdot h$$

d - density
g - acc. of gravity

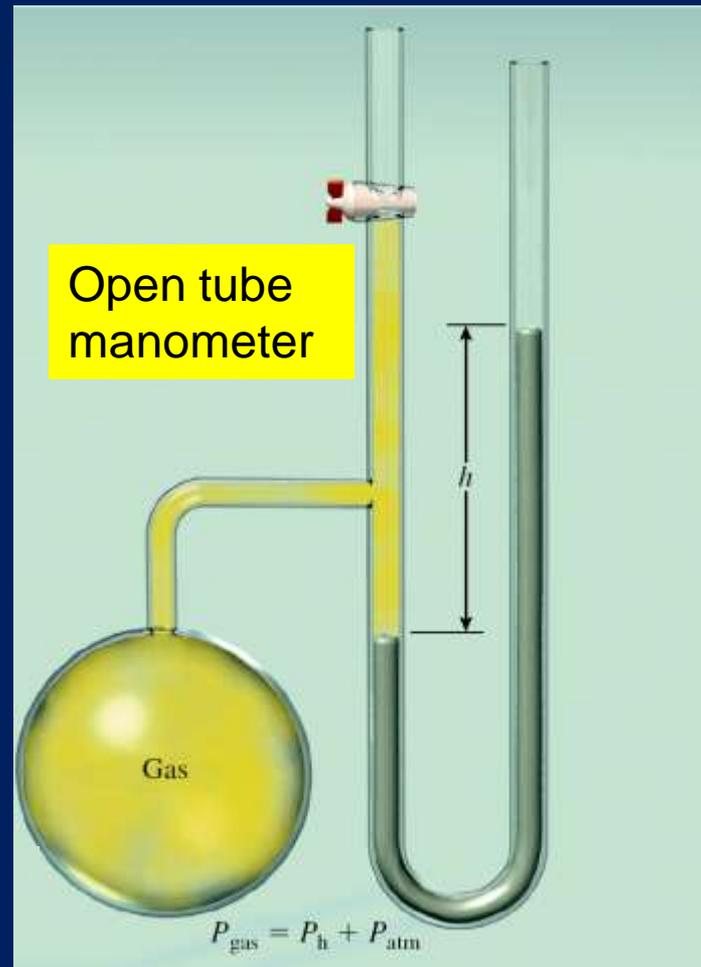
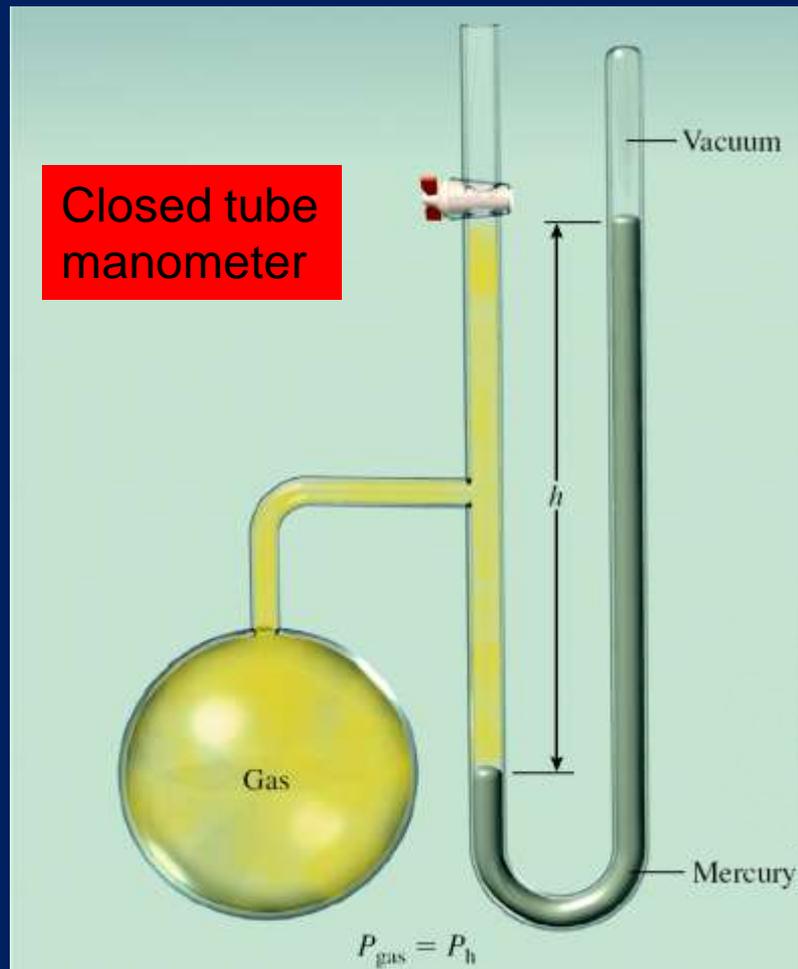
atmospheric pressure



atmospheric pressure

Manometer

Device for Measuring the Pressure of a confined gas



11.2 The Gas Laws

- **Gas laws – empirical relationships among gas parameters**
 - **Volume (V)**
 - **Pressure (P)**
 - **Temperature (T)**
 - **Amount of a gas (n)**

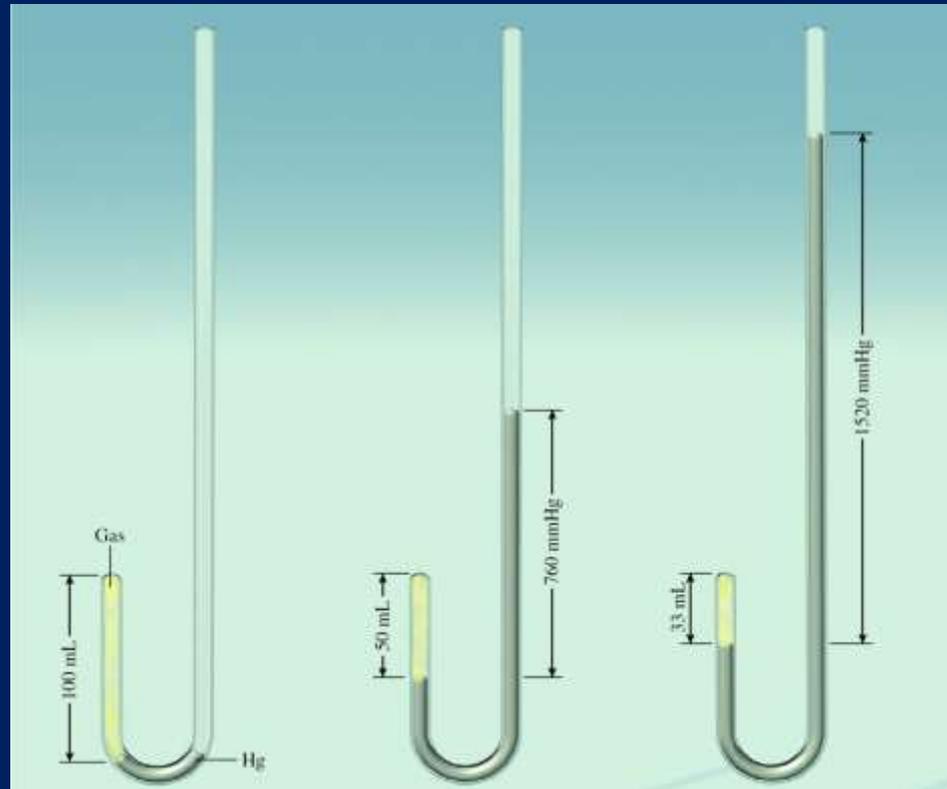
5.2 The Gas Laws of Boyle, Charles and Avogadro

- Boyle's Law: $PV = \text{const}$
 - at constant n, T
- Charles' Law: $V/T = \text{const}$
 - at constant n, P
- Avogadro's Law: $V/n = \text{const}$
 - at constant P, T

Boyle's law

pressure-volume relationship at constant temperature

$$P_1V_1=P_2V_2$$

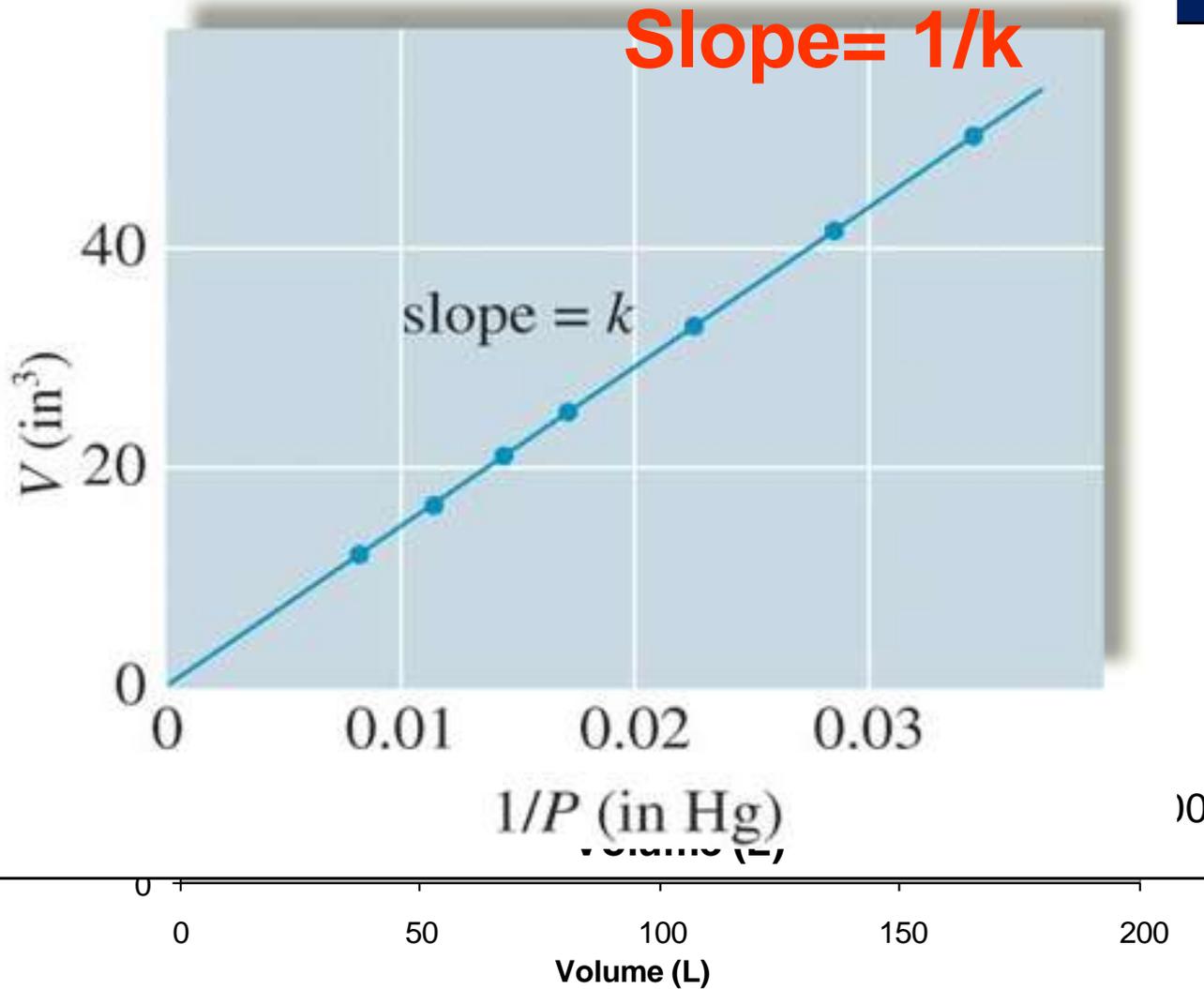


Boyle's Law

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

$PV = k$
(at constant
T and n)

$$P_1 V_1 = P_2 V_2$$



Charles's Law

- $V/T = b$

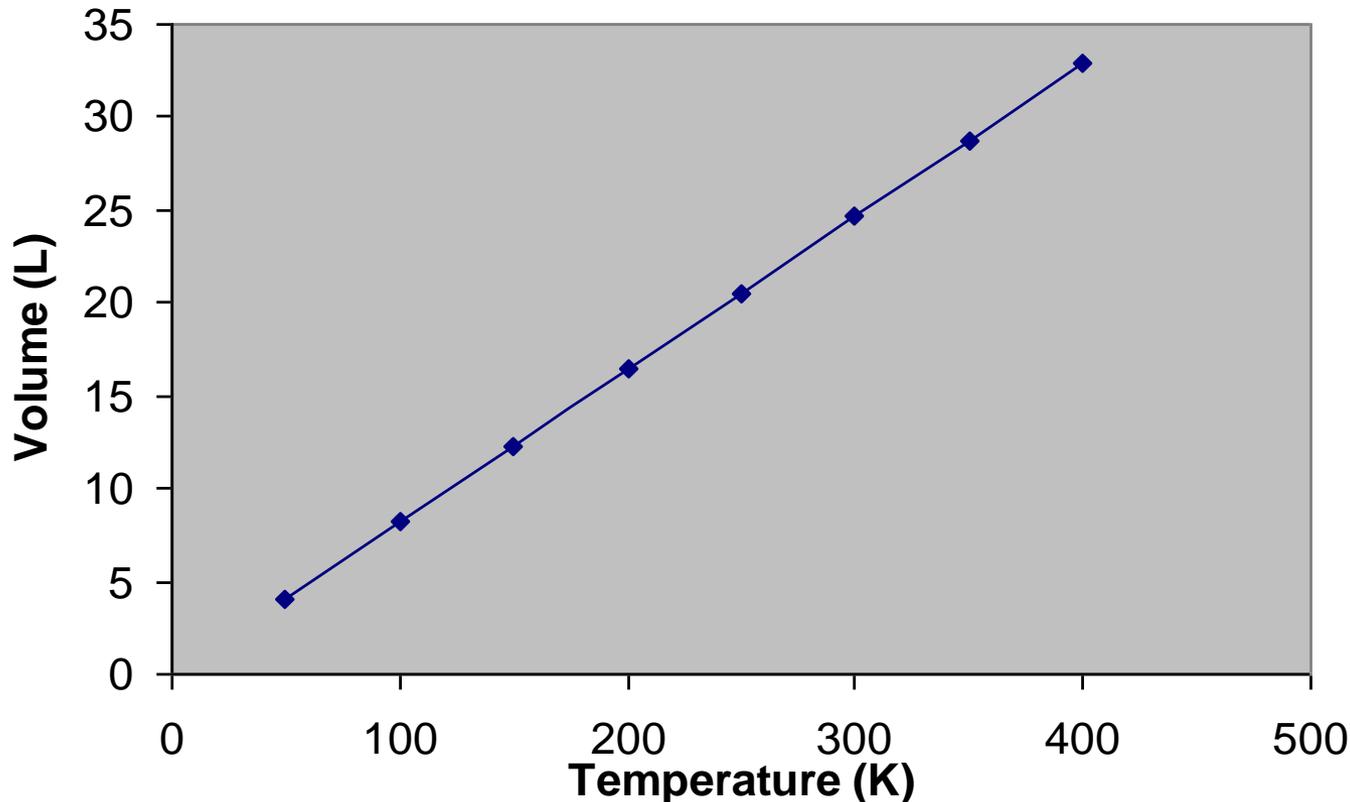
- $V = bT$

(constant P & n)

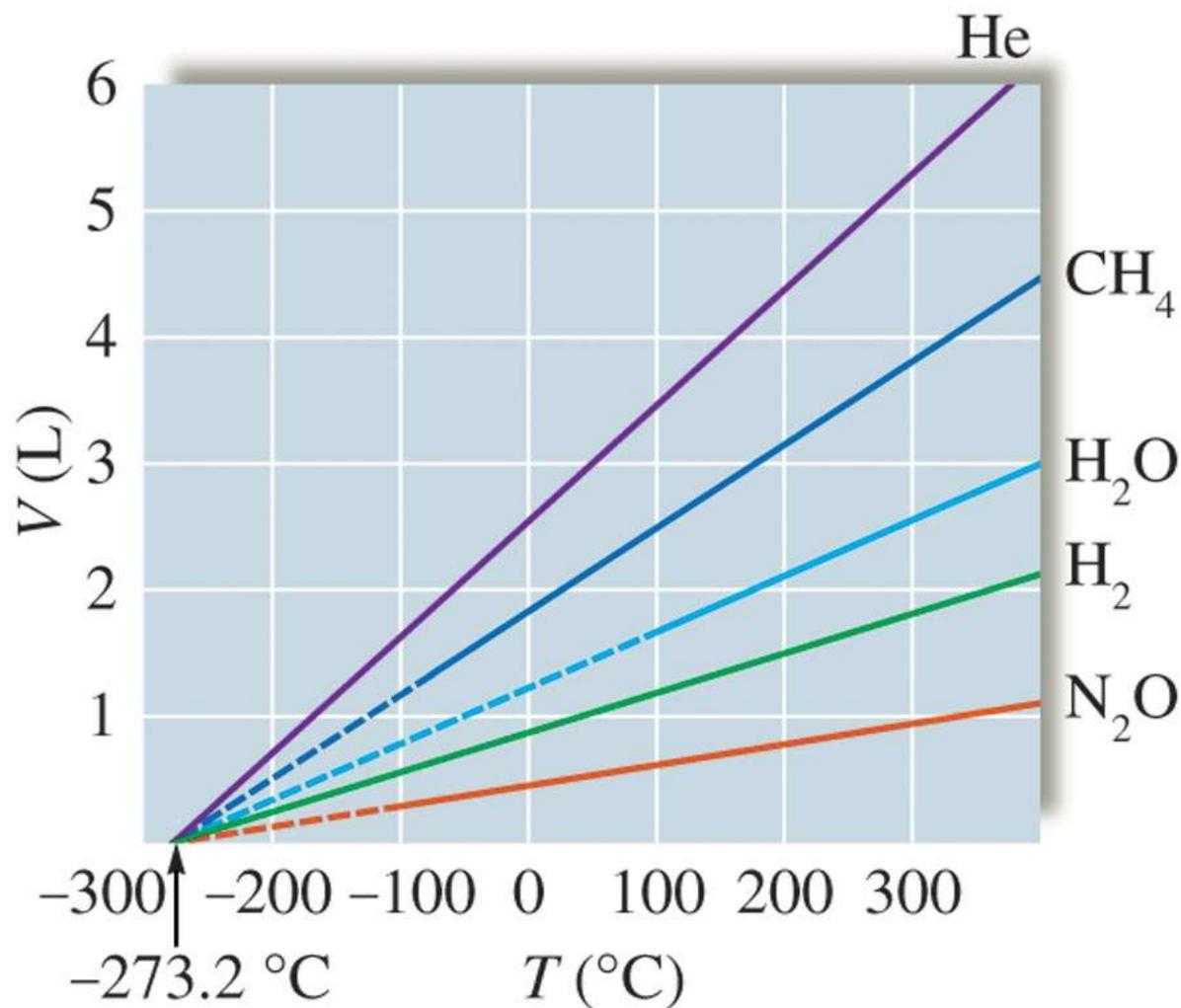
temperature-volume relationship at constant pressure

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

Charles' Law



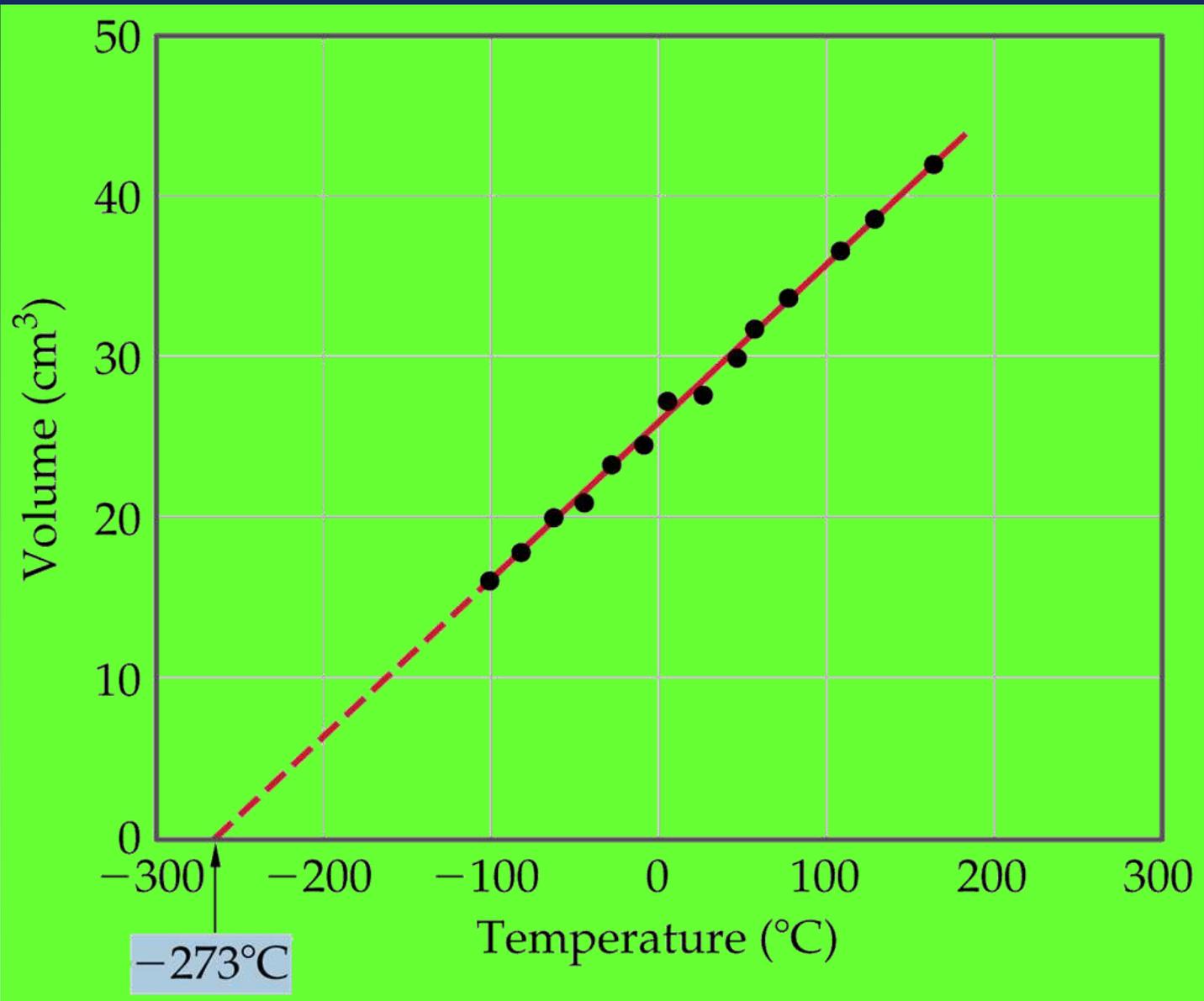
Plots of V Versus T(Celsius) for Several Gases



Volume of a gas
Changes by $\frac{1}{273}$

When the temp.
Changes by
 1°C .

I.e., at -273°C ,
 $V=0$???

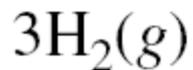


All gases will solidify or liquefy before reaching zero volume.

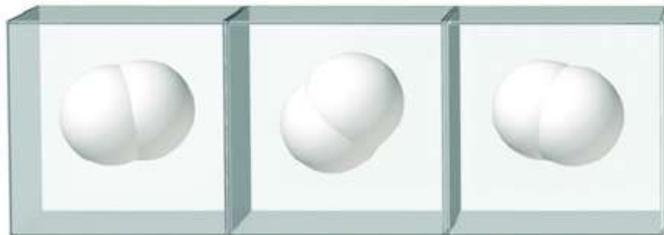
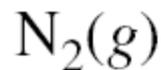
Avogadro's law

The volume of a gas sample is directly proportional to the number of moles in the sample at constant pressure and temperature

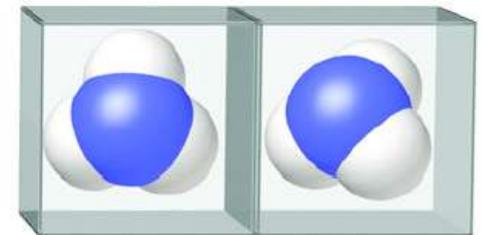
$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$



+



+



3 molecules

+

1 molecule



2 molecules

3 moles

+

1 mole



2 moles

3 volumes

+

1 volume



2 volumes

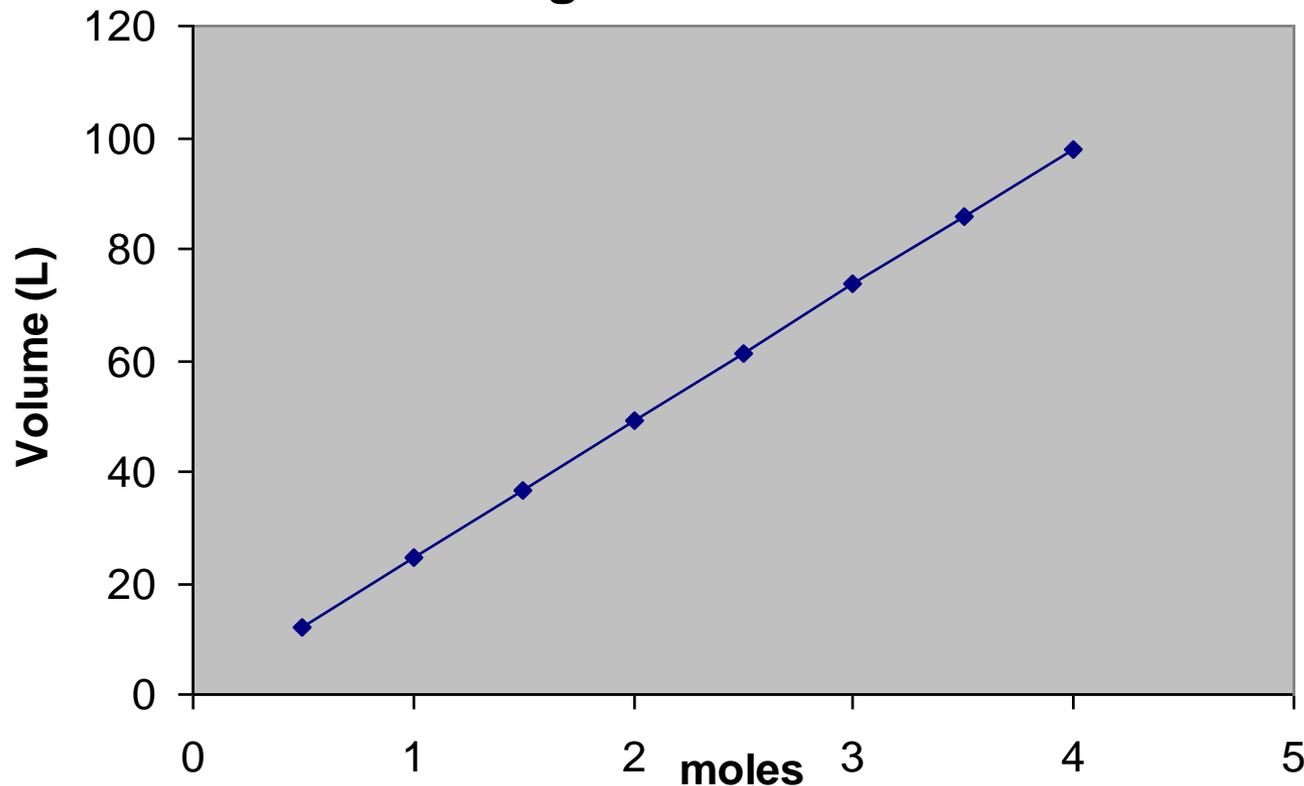
Avogadro's Law

- $V \propto n$
- $V = an$

(constant P & T)

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

Avogadro's Law



How will the volume of a given gas change if the quantity of gas, absolute temperature, and pressure, all double?

Avogadro

× 2

Charles

× 2

Boyle

× 1/2

$$2 \times 2 \times \frac{1}{2} = 2$$

⇒ volume doubles

11.3 The Ideal Gas Law

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

Boyle's law

$$V \propto T$$

Charles's law

$$V \propto n$$

Avogadro's law

Universal gas
constant

$$V = R \left(\frac{nT}{P} \right)$$



$$PV = nRT$$

The Ideal Gas Law

$$PV = nRT$$



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

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

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

The Ideal Gas Law can be used to derive the gas laws as needed!

The value of R

- What is **R** for 1.00 mol of an ideal gas at **STP** (0 °C and 1.00 atm)? Given that **V of 1 mol of gas at STP = 22.4L**

$$PV = nRT$$

$$R = \frac{PV}{nT}$$

$$R = 0.0821 \frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}}$$

$$R = 0.0821 \text{ atm L mol}^{-1} \text{ K}^{-1}$$

The Ideal Gas Law: Final and initial state problems

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

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad (\text{Ideal gas equation})$$

A steel cylinder with a volume of 68.0 L contains O₂ at a pressure of 15,900 kPa at 23°C. What is the volume of this gas at STP?

$$P_1 = 15,900 \text{ kPa} \times \frac{1 \text{ atm}}{101.3 \text{ kPa}} = 157.0 \text{ atm}$$

$$P_2 = 1 \text{ atm}$$

$$T_1 = 23 + 273 = 296 \text{ K}$$

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

$$V_1 = 68.0 \text{ L}$$

$$V_2 = ?$$

$$PV = nRT \Rightarrow$$

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

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

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

$$= \frac{(157.0 \text{ atm})(68.0 \text{ L})(273 \text{ K})}{(296 \text{ K})(1 \text{ atm})} = 9850 \text{ L}$$

TABLE 11.4Various Equivalent Expressions of the Gas Constant, R

Numerical Value	Unit
0.08206	L · atm/K · mol
62.36	L · torr/K · mol
0.08314	L · bar/K · mol
8.314	m ³ · Pa/K · mol
8.314	J/K · mol
1.987	cal/K · mol

Note that the product of volume and pressure gives units of *energy* (i.e., joules and calories).

Molar Volume

At STP

4.0 g He
1 mole
(STP)

$V = 22.4 \text{ L}$

16.0 g CH₄
1 mole
(STP)

$V = 22.4 \text{ L}$

44.0 g CO₂
1 mole
(STP)

$V = 22.4 \text{ L}$

For an ideal gas, calculate the pressure of the gas if 0.215 mol occupies 338 mL at 32.0°C.

$$n = 0.215 \text{ mol}$$

$$V = 338 \text{ mL} = 0.338 \text{ L}$$

$$T = 32.0 + 273.15 = 305.15 \text{ K}$$

$$P = ?$$

$$PV = nRT \Rightarrow$$

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

$$P = \frac{(0.215 \text{ mol}) \left(0.08206 \frac{\text{L} \times \text{atm}}{\text{mol} \times \text{K}} \right) (305.15 \text{ K})}{0.338 \text{ L}}$$

$$= 15.928$$

$$= 15.9 \text{ atm}$$

- Applications of the ideal gas equation
 - Relation to density (d)

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

density

$$\mathcal{M} \times \frac{n}{V} = \frac{P}{RT} \times \mathcal{M}$$

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

- Relation to molar mass (\mathcal{M})

$$\mathcal{M} = \frac{dRT}{P}$$

Molar mass of a gas

$$P \times V = n \times R \times T$$

$$n = \frac{m}{M}$$

- $P \times V = \frac{m \times R \times T}{M}$
- m = mass, in grams
- M = molar mass, in g/mol
- Molar mass = $\frac{m R T}{P V}$

Example

A glass vessel weighs 40.1305 g when clean, dry and evacuated; it weighs 138.2410 when filled with water at 25°C ($d=0.9970 \text{ g cm}^{-3}$) and 40.2959 g when filled with propylene gas at 740.3 mm Hg and 24.0°C. What is the molar mass of polypropylene?

$$PV = nRT$$

\Rightarrow

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

$$M = \frac{mRT}{PV}$$

Volume of the vessel



$$V_{\text{flask}} \frac{m_{\text{H}_2\text{O}}}{d_{\text{H}_2\text{O}}} = \frac{138.2410 \text{ g} - 40.1305 \text{ g}}{(0.9970 \text{ g cm}^{-3})}$$
$$= 98.41 \text{ cm}^3 = 0.09841 \text{ L}$$

$$m_{\text{gas}} = m_{\text{filled}} - m_{\text{empty}} = (40.2959 \text{ g} - 40.1305 \text{ g})$$
$$= 0.1654 \text{ g}$$

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

$$M = \frac{(0.6145 \text{ g})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(297.2 \text{ K})}{(0.9741 \text{ atm})(0.09841 \text{ L})}$$

$$M = 42.08 \text{ g/mol}$$

Density

- Density (d) is mass divided by volume

- $P \times V = \frac{m \times R \times T}{M}$

- $P = \frac{m \times R \times T}{V \times M}$

- $d = \frac{m}{V}$

- $P = \frac{d \times R \times T}{M}$



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

Example

Calculate the density in g/L of O₂ gas at STP.

From STP, we know the P and T.

$$P = 1.00 \text{ atm} \quad T = 273 \text{ K}$$

Rearrange the ideal gas equation for moles/L

$$d = \frac{PXM}{R \times T}$$

$$d = \frac{PXM}{RXT}$$

$$d = \frac{(1.00 \text{ atm}) \times (32.0 \frac{\text{g}}{\text{mol}})}{(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}) \times (273\text{K})} = 1.43 \text{ g / L}$$

**The density of O₂ gas at STP is
1.43 grams per liter**

Example

- 2.00 g sample of $SX_6(g)$ has a volume of 329.5 Cm^3 at 1.00 atm and 20°C . Identify the element X. Name the compound
- $P = 1.00 \text{ atm}$

$$V = 329.5 \text{ Cm}^3 \times \frac{1\text{L}}{1000\text{Cm}^3} = 0.3295 \text{ L}$$

- $T = 273 + 20 = 293\text{K}$

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

$$MM = \frac{(2.00 \text{ g})(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}})(293 \text{ K})}{(1.00 \text{ atm})(0.3295 \text{ L})}$$

$$= 146 \text{ g SX}_6 / \text{mol}$$

Molar mass of (X₆) = 146 - 32 = 114 g/mol

Molar mass of X = (114 g/mol X₆)/6 = 19

X = with a molar mass of 19 = F

The compound is SF₆

$$d = \frac{PXM}{RXT}$$

$$d = \frac{(1.00 \text{ atm}) \times (32.0 \frac{\text{g}}{\text{mol}})}{(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}) \times (273\text{K})} = 1.43 \text{ g / L}$$

**The density of O₂ gas at STP is
1.43 grams per liter**

Example

- 2.00 g sample of $SX_6(g)$ has a volume of 329.5 Cm^3 at 1.00 atm and 20°C . Identify the element X. Name the compound
- $P = 1.00 \text{ atm}$

$$V = 329.5 \text{ Cm}^3 \times \frac{1\text{L}}{1000\text{Cm}^3} = 0.3295 \text{ L}$$

- $T = 273 + 20 = 293\text{K}$

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

$$MM = \frac{(2.00 \text{ g})(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}})(293 \text{ K})}{(1.00 \text{ atm})(0.3295 \text{ L})}$$

$$= 146 \text{ g SX}_6 / \text{mol}$$

Molar mass of (X₆) = 146^f - 32 = 114 g/mol

Molar mass of X = (114 g/mol X₆) / 6 = 19

X = with a molar mass of 19 = F

The compound is SF₆

11.4 Reactions with Gaseous Reactants and Products

- Amounts of gaseous reactants and products can be calculated by utilizing
 - The ideal gas law to relate moles to T, P and V.
 - Moles can be related to mass by the molar mass
 - The coefficients in the balance equation to relate moles of reactants and products
 - **Standard Temperature and Pressure (STP):**
0°C and 1 atm
 - **1 mole of gas occupies 22.4 L at STP.**

Carbon monoxide reacts with oxygen to form carbon dioxide according to the equation:



What volume of O_2 is required to completely react with 65.8 mL of CO at constant temperature and pressure?

Use the fact that mL of reactant are proportional to moles of reactant.

$$65.8 \text{ mL of CO} \times \frac{1 \text{ mL of O}_2}{2 \text{ mL of CO}} = 32.9 \text{ mL O}_2$$

Magnesium is an active metal that replaces hydrogen from an acid by the following reaction:



How many g of Mg are needed to produce 5.0 L of H₂ at a temperature of 25 °C and a pressure of 745 mmHg?



Hint: find moles of H₂ using PV = nRT then work as a stoichiometry problem.

$$n = \frac{PV}{RT} = \frac{745 \text{ mmHg} \cdot 5.0 \text{ L}}{62.4 \text{ L}\cdot\text{mmHg} \cdot 298 \text{ K}} \cdot \frac{\text{mol}\cdot\text{K}}{\text{mol}\cdot\text{K}}$$

$$n = 0.20 \text{ mol}$$

Example

- 30.2 mL of 1.00 M HCl are reacted with excess FeS. What volume of gas is generated at STP?



moles HCl = Vol (L) X M



$$0.0302 \text{ L} \cdot \frac{1.00 \text{ mol HCl}}{\text{L}} \cdot \frac{\text{mol H}_2\text{S}}{2 \text{ mol HCl}} \left(\frac{0.0821 \text{ atm L}}{\text{mol K}} \right) (273.15 \text{ K})$$

$$= 0.339 \text{ L}$$

$$PV = nRT$$

$$V = nRT/P$$

Example

The decomposition of sodium azide, NaN_3 , at high temperatures produces $\text{N}_2(\text{g})$. What volume of $\text{N}_2(\text{g})$, measured at 735 mm Hg and 26°C , is produced when 70.0 g NaN_3 is decomposed.





Determine moles of N₂:

$$n_{\text{N}_2} = 70 \text{ g NaN}_3 \times \frac{1 \text{ mol NaN}_3}{65.01 \text{ g N}_3/\text{mol N}_3} \times \frac{3 \text{ mol N}_2}{2 \text{ mol NaN}_3} = 1.62 \text{ mol N}_2$$

Determine volume of N₂:

$$V = \frac{nRT}{P} = \frac{(1.62 \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(299 \text{ K})}{\left\{ (735 \text{ mm Hg}) \frac{1.00 \text{ atm}}{760 \text{ mm Hg}} \right\}}$$
$$= 41.1 \text{ L}$$

- **Relation of changes in pressure to moles in a reaction**

- **Example**

- **At constant temperature and volume**

$$n = P \times \left(\frac{V}{RT} \right)$$

$$\Delta n = \Delta P \times \left(\frac{V}{RT} \right)$$

11.5 Gas Mixtures

- In gaseous mixtures, each gas behaves as if it occupies the container alone.
 - Assuming no reaction between gases
- *partial pressure* (P_i): the pressure exerted by each gas in a gaseous mixture

Dalton's law of partial pressure

- The total pressure is the sum of the partial pressures.
- $P_{\text{Total}} = P_1 + P_2 + P_3 + P_4 + P_5 \dots$

$$P_t = \sum P_i$$

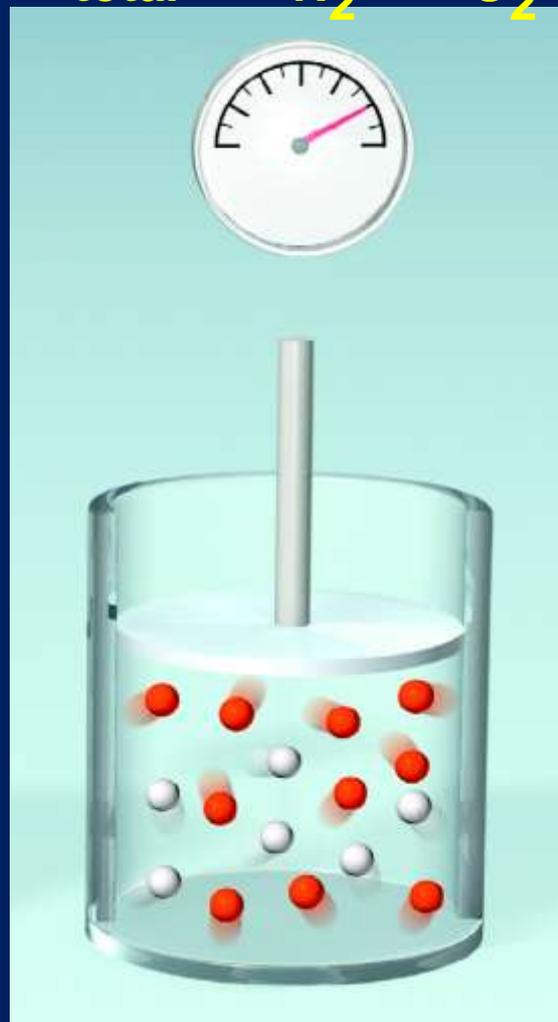
Schematic of Dalton's Law

$$P_{N_2}$$



Add O_2
→

$$P_{\text{total}} = P_{N_2} + P_{O_2}$$



$$P_{\text{Total}} = P_1 + P_2 + P_3 + P_4 + P_5 \dots$$

$$\text{➤ } P_{\text{Total}} = \frac{n_1 RT}{V} + \frac{n_2 RT}{V} + \frac{n_3 RT}{V} + \dots$$

➤ In the same container R, T and V are the same.

$$\text{➤ } P_{\text{Total}} = (n_1 + n_2 + n_3 + \dots) \frac{RT}{V}$$

Thus,

$$P_{\text{Total}} = n_{\text{Total}} \left(\frac{RT}{V} \right)$$

A 250.0 mL flask contains 1.00 mg of He and 2.00 mg of H₂ at 25.0°C. Calculate the total gas pressure in the flask in atmospheres.

The total pressure is due to the partial pressures of each of these gases.

so:

$$P_{\text{total}} = P_{\text{He}} + P_{\text{H}_2} = (n_{\text{He}} + n_{\text{H}_2}) \left(\frac{RT}{V} \right)$$

For He:

$$\frac{1.00 \times 10^{-3} \text{ g He}}{4.00 \text{ g}} = 2.50 \times 10^{-4} \text{ mol He}$$

For H₂:

$$\frac{2.00 \times 10^{-3} \text{ g H}_2}{2.016 \text{ g}} = 9.92 \times 10^{-4} \text{ mol H}_2$$

The mole fraction

- Mole fraction: number of moles of one component in a mixture relative to the total number of moles in the mixture
- symbol is Greek letter chi χ

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

Mole fraction expressed in pressures

$$\chi = \frac{n_1}{n_{Total}} = \frac{n_1}{n_1 + n_2 + n_3 + \dots}$$

$$n_1 = P_1 \left(\frac{V}{RT} \right); n_2 = P_2 \left(\frac{V}{RT} \right); \dots\dots\dots$$

$$\chi_1 = \frac{n_1}{n_{Total}} = \frac{P_1 \left(\frac{V}{RT} \right)}{P_1 \left(\frac{V}{RT} \right) + P_2 \left(\frac{V}{RT} \right) + P_3 \left(\frac{V}{RT} \right) + \dots\dots}$$

$$\chi_1 = \frac{\cancel{P_1 \left(\frac{V}{RT} \right)}}{\left(\frac{V}{RT} \right) (P_1 + P_2 + P_3 + \dots)}$$

$$\chi_1 = \frac{P_1}{(P_1 + P_2 + P_3 + \dots)} = \frac{P_1}{P_{Total}}$$

$$\chi_i = \frac{n_i}{n_{Total}} = \frac{P_i}{P_{Total}}$$

$$P_i = \chi_i P_{Total}$$

Example

- A 1.00 L sample of dry air at 786 Torr and 25 °C contains 0.925 g N₂ plus other gasses (such as O₂, Ar and CO₂.) a) What is the partial pressure of N₂? b) What is the mole fraction of N₂?

$$0.925 \text{ g} \cdot \frac{\text{mol}}{28.0 \text{ g}} = 0.0330 \text{ mol}$$

$$PV = nRT$$
$$P = nRT/V$$

$$\frac{(0.0330 \text{ mol})(0.0821 \text{ atm L mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{1.00 \text{ L}} = 0.807 \text{ atm}$$

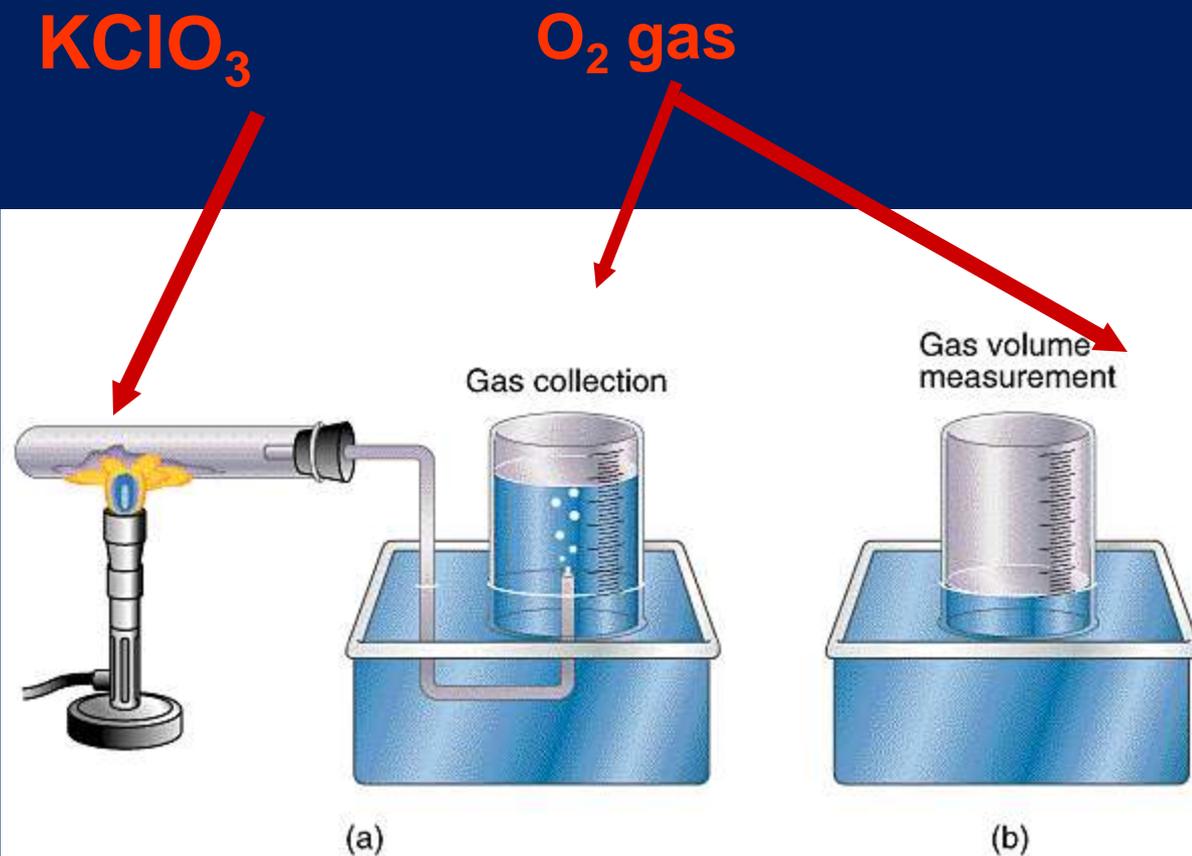
$$P_N = \chi_N P_{\text{Total}}$$

$$0.807 \text{ atm} \cdot \frac{760 \text{ Torr}}{\text{atm}} = 613 \text{ Torr}$$

$$X_{N_2} = \frac{613 \text{ Torr}}{786 \text{ Torr}} = 0.780$$

Collecting gas over water

An insoluble gas is passed into a container of water, the gas rises because its density is much less than that of water and the water must be displaced



Collection of Gases over Water

Assuming the gas is saturated with water vapor, the partial pressure of the water vapor is the *vapor pressure* of the water.

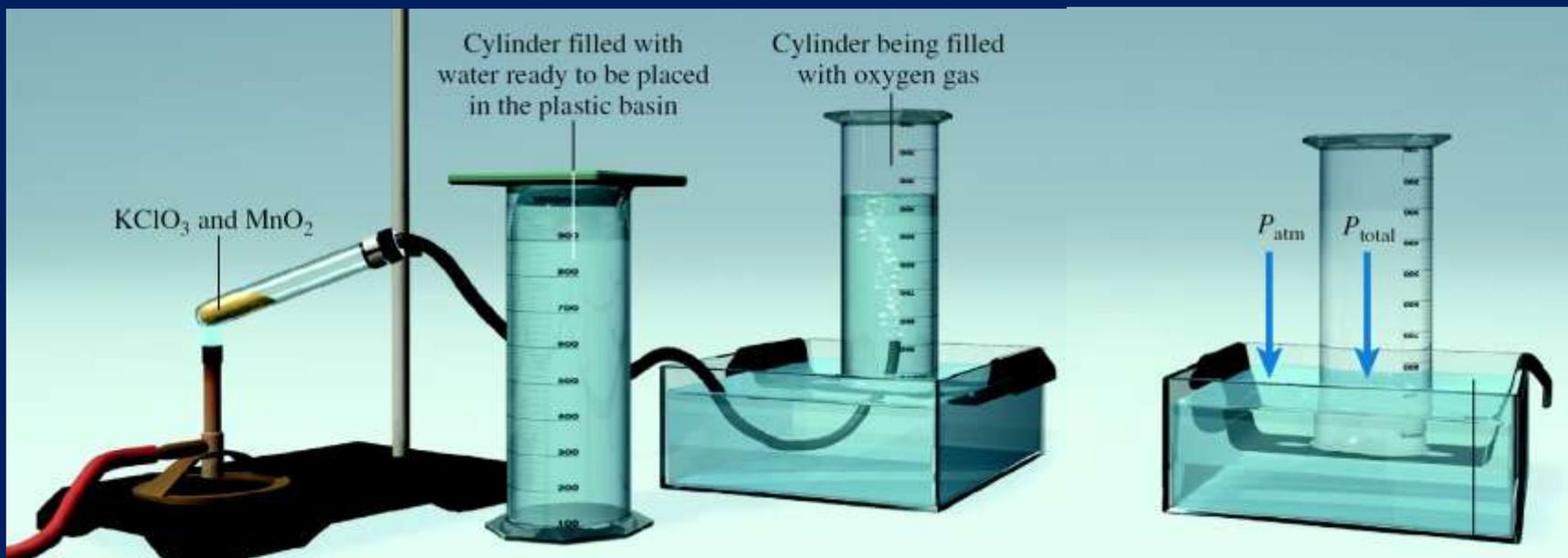
$$P_{\text{total}} = P_{\text{gas}} + P_{\text{H}_2\text{O}(\text{g})}$$

$$P_{\text{gas}} = P_{\text{total}} - P_{\text{H}_2\text{O}(\text{g})}$$

Oxygen was produced and collected over water at 22°C and a pressure of 754 torr.



325 mL of gas were collected and the vapor pressure of water at 22°C is 21 torr. Calculate the number of moles of O₂ and the mass of KClO₃ decomposed.



$$P_{\text{total}} = P_{\text{O}_2} + P_{\text{H}_2\text{O}} = P_{\text{O}_2} + 21 \text{ torr} = 754 \text{ torr}$$

$$P_{\text{O}_2} = 754 \text{ torr} - 21 \text{ torr} = 733 \text{ torr} = 733 / 760 \text{ atm}$$

$$V = 325 \text{ mL} = 0.325 \text{ L}$$

$$T = 22^\circ\text{C} + 273 = 295 \text{ K}$$

$$n = \frac{PV}{RT}$$

$$n_{\text{O}_2} = \frac{\left(\frac{733}{760} \text{ atm}\right)(0.325 \text{ L})}{\left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(295 \text{ K})} = 1.29 \times 10^{-2} \text{ mol O}_2$$



$$1.29 \times 10^{-2} \text{ mol O}_2 \left(\frac{2 \text{ mol KClO}_3}{3 \text{ mol O}_2} \right) \left(\frac{122.6 \text{ g KClO}_3}{1 \text{ mol KClO}_3} \right) = 1.06 \text{ g KClO}_3$$

A 250.0 mL flask contains 1.00 mg of He and 2.00 mg of H₂ at 25.0°C. Calculate the total gas pressure in the flask in atmospheres.

so:

$$P_{\text{total}} = P_{\text{He}} + P_{\text{H}_2} = (n_{\text{He}} + n_{\text{H}_2}) \left(\frac{RT}{V} \right)$$

$$\text{For He: } \frac{1.00 \times 10^{-3} \text{ g He}}{4.00 \text{ g}} \text{ mol} = 2.50 \times 10^{-4} \text{ mol He}$$

$$\text{For H}_2: \frac{2.00 \times 10^{-3} \text{ g H}_2}{2.016 \text{ g}} \text{ mol} = 9.92 \times 10^{-4} \text{ mol H}_2$$

$$\text{And: } P_{\text{total}} = (2.50 \times 10^{-4} + 9.92 \times 10^{-4})(RT/V)$$

$$= \frac{(0.001242 \text{ mol})(0.0821 \text{ L}\cdot\text{atm})(25 + 273)\text{K}}{\text{mol}\cdot\text{K} (0.2500 \text{ L})}$$

$$P_{\text{total}} = 0.1216 \text{ atm}$$

11.6 The Kinetic Molecular Theory

- **It explains why ideal gases behave the way they do.**
- **Postulates of the kinetic Theory:**
 - A gas is composed of particles that are separated by relatively large distances. The volume occupied by individual molecules is negligible.
 - Gas molecules are constantly in random motion, moving in straight paths, colliding with the walls of their container and with one another in perfectly elastic collisions.
 - Gas particles exert no attractive or repulsive forces on one another.
 - The average kinetic energy of the particles is proportional to the absolute temperature.

Application of KMT to the gas laws

KMT explains ideal gas laws

- **Compressibility:** gases are compressible because the gas molecules are separated by large distances.
- **P&V:** $P = (nRT) \cdot (1/V) \Rightarrow P \propto 1/V$ (Boyle's law)
 - When V decreases # collisions increases
- **P & T:** $P = (nR/V) \cdot T \Rightarrow P \propto T$
 - When T increases, hits with walls become stronger and more frequent
- **V & T:** $V = (nR/P) \cdot T \Rightarrow V \propto T$ (Charle's law)
 - When T increases hits with walls become stronger and more frequent. To keep P constant, V must increase to compensate for particles speeds

- **V & n : $V = (RT/P) \cdot N \Rightarrow V \propto n$ (Avogadro's law)**
 - To maintain constant P and T , as V increases n must increase
 - When n increase P would increase if the volume is kept constant. V must increase to return P to its original value
- **$P_{\text{total}} = \sum P_i$ (Dalton's law)**
 - Individual particles are independent of each other and their volumes are negligible. Thus identities of gas particles do not matter and would be treated as if they belong to one gas

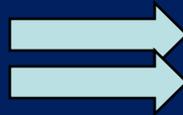
• Molecular speed

- Total kinetic energy of a mole of gas is $\frac{3}{2} RT$
- The average kinetic energy of one molecule is $\frac{1}{2} m \overline{u^2}$
- The average kinetic energy for one mole of gas molecules is (N_A is Avogadro's number)

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

- **Because $m \times N_A = \text{molar mass} = M$**

$$\overline{u^2} = \frac{3RT}{M}$$



$$\sqrt{\overline{u^2}} = \sqrt{\frac{3RT}{M}}$$

– **Root mean square (rms) speed (u_{rms})**

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

Where M is the molar mass in kg/mole, and R has the units 8.3145 J/Kmol.
The velocity will be in m/s

How fast do N₂ molecules move at room temperature (25°C)?

$$u = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \left(8.314 \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2 \text{ mol K}} \right) (298 \text{ K})}{28.0 \times 10^{-3} \frac{\text{kg}}{\text{mol}}}} = 515 \frac{\text{m}}{\text{s}} = 1150 \text{ mph}$$

- For two gases 1 and 2

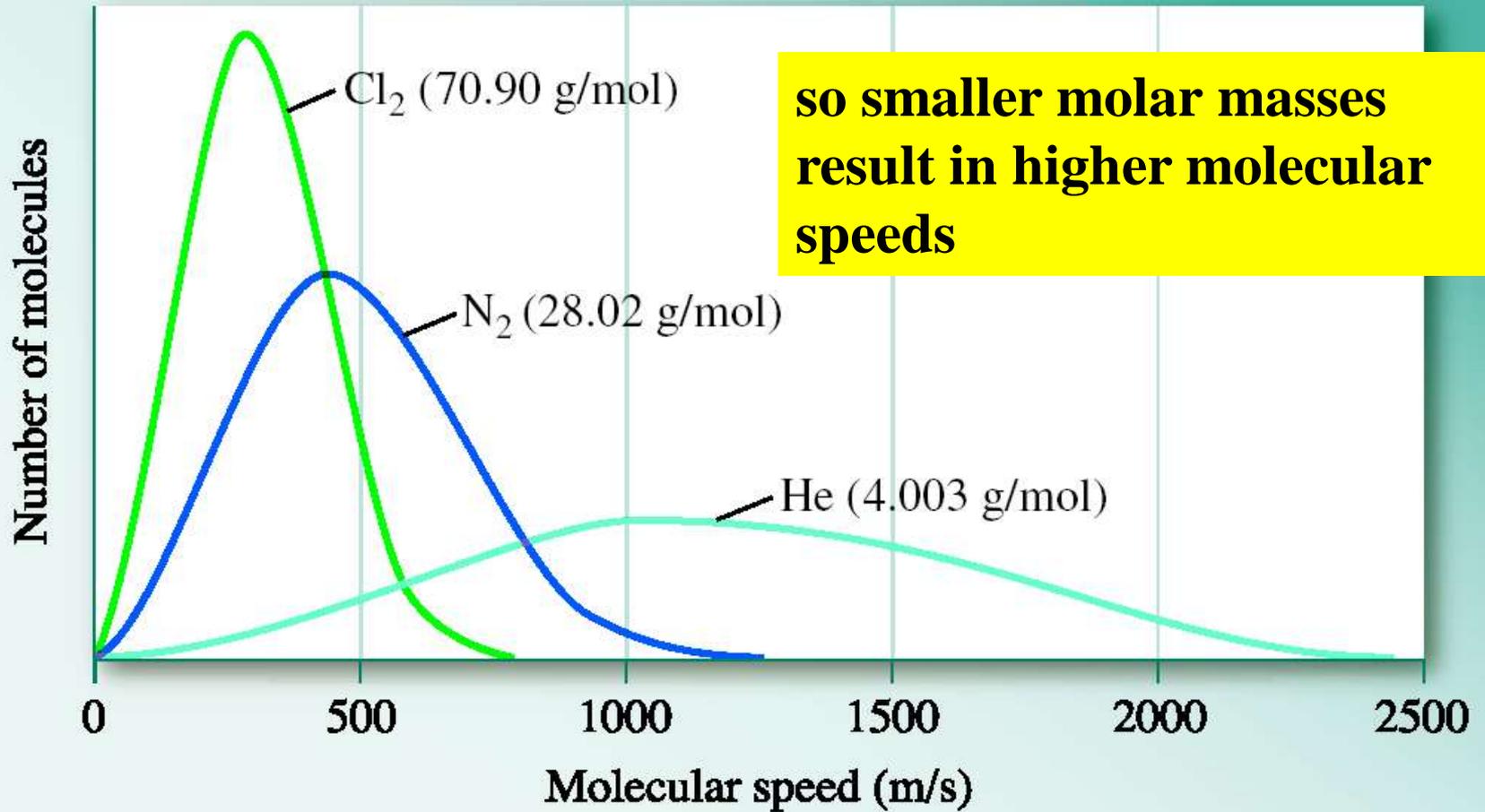
$$\frac{u_{\text{rms } 1}}{u_{\text{rms } 2}} = \frac{\sqrt{\frac{3RT}{M_1}}}{\sqrt{\frac{3RT}{M_2}}} = \sqrt{\frac{M_2}{M_1}}$$

- Thus,

$$\frac{u_{\text{rms } 1}}{u_{\text{rms } 2}} = \sqrt{\frac{M_2}{M_1}}$$

Effect of Molar Mass on Molecular Speed

$T = 300\text{ K}$



Molecular speed for same gas at two different temperatures

$$u_{T_1} = \left(\frac{3RT_1}{M} \right)^{1/2}$$

$$u_{T_2} = \left(\frac{3RT_2}{M} \right)^{1/2}$$

$$\frac{u_{T_1}}{u_{T_2}} = \left(\frac{T_1}{T_2} \right)^{1/2}$$

Molecular speed for two different gases at two different temperatures

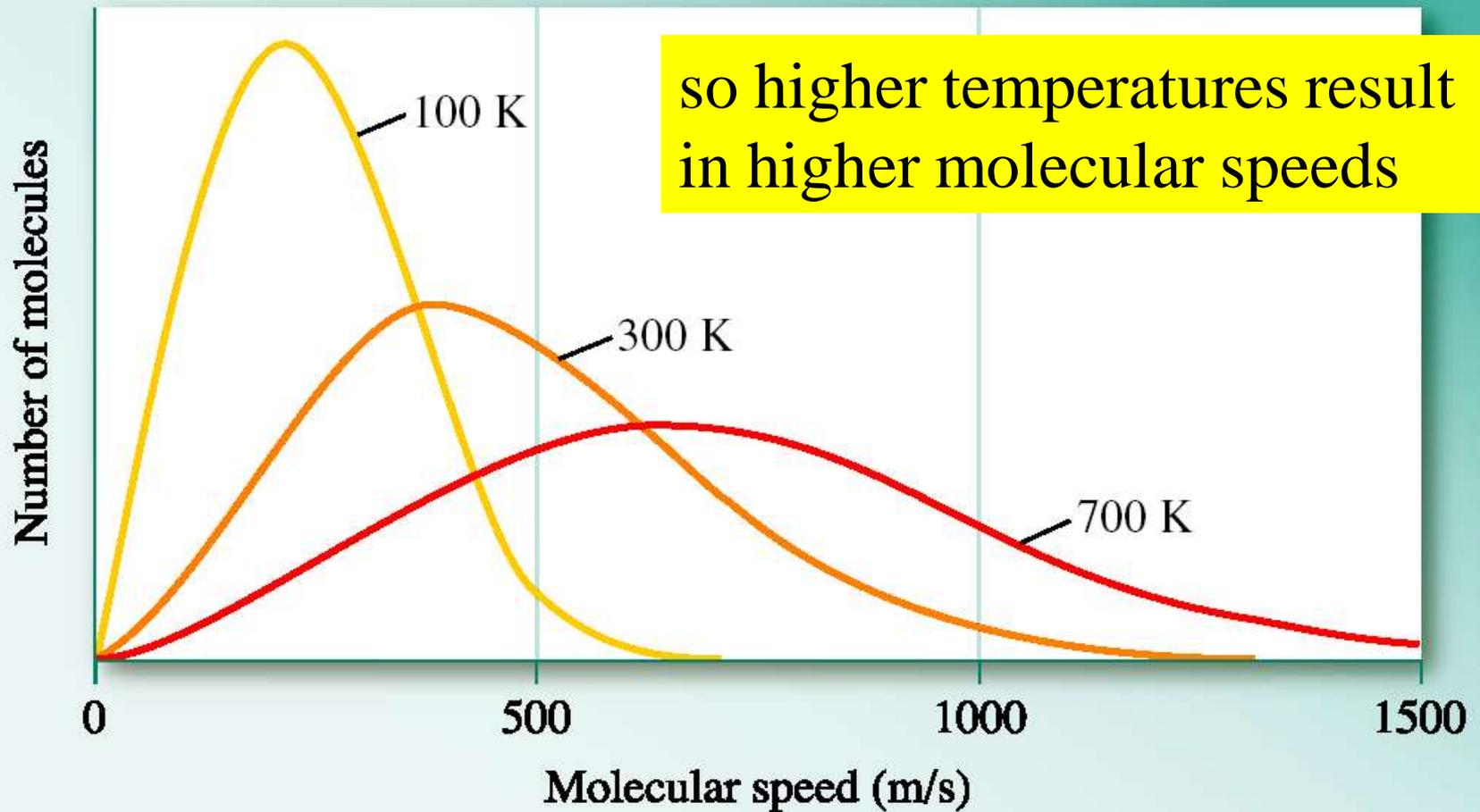
$$u_{T_1} = \left(\frac{3RT_1}{M_1} \right)^{1/2}$$

$$u_{T_2} = \left(\frac{3RT_2}{M_2} \right)^{1/2}$$

$$\frac{u_{T_1}}{u_{T_2}} = \left(\frac{T_1 M_2}{T_2 M_1} \right)^{1/2}$$

Effect of Temperature on Molecular Speed

N_2 (28.02 g/mol)



- Comparison of rms and other speed measurements
 - Mean or average speed (u_{avg})
 - Most probable speed (u_{mp})
 - Rms speed (u_{rms})

Example: Assume five speeds: 2, 4, 4, 6 and 8 m/s

$$u_{\text{avg}} = \frac{2+4+4+6+8}{5} = \frac{24}{5} = 4.8 \text{ m/s}$$

$$u_{\text{mp}} = 4.0 \text{ m/s}$$

$$u_{\text{rms}} = \sqrt{\frac{2^2 + 4^2 + 4^2 + 6^2 + 8^2}{5}} = \sqrt{\frac{136}{5}} = 5.2 \text{ m/s}$$

Place the following gases in order of increasing r.m.s. speed at 300 K,

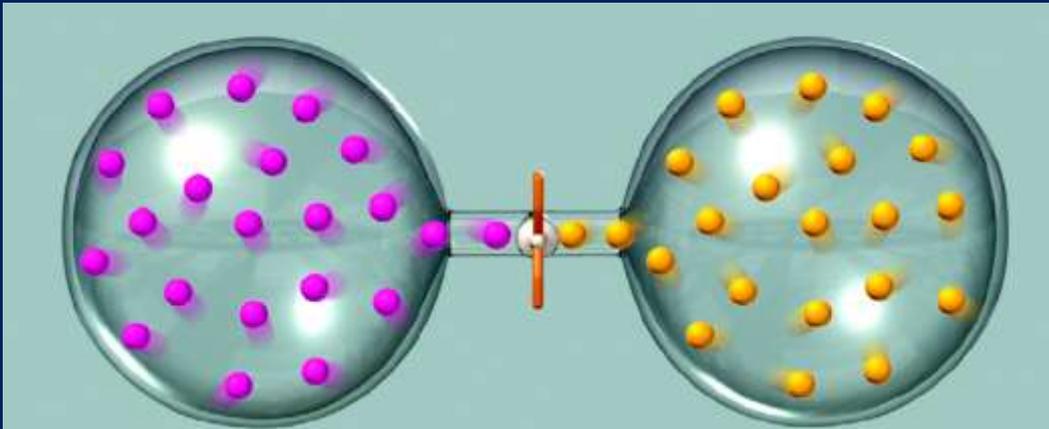
H_2 , CO_2 , Ne, NH_3 , Cl_2

$$u_{\text{Cl}_2} < u_{\text{CO}_2} < u_{\text{Ne}} < u_{\text{NH}_3} < u_{\text{H}_2}$$

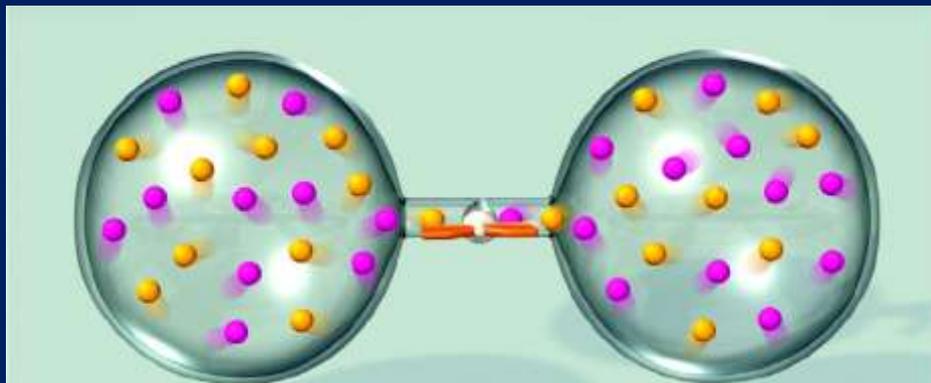
Which one has the highest average kinetic energy?

At the same temperature, all have the same average kinetic energy.

- **Diffusion:**
- **Mixing of gases as a results of random motion and collisions.**



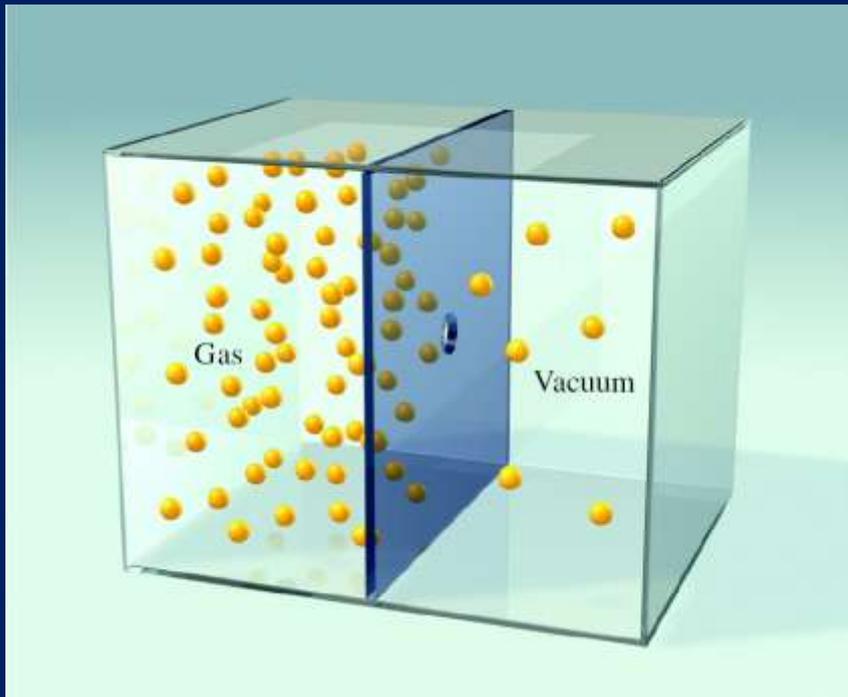
Open valve



$$\text{Rate} \propto \frac{1}{\sqrt{M}}$$

Effusion

- The escape of a gas from a container to a region of vacuum



$$\text{Rate} \propto \frac{1}{\sqrt{M}}$$

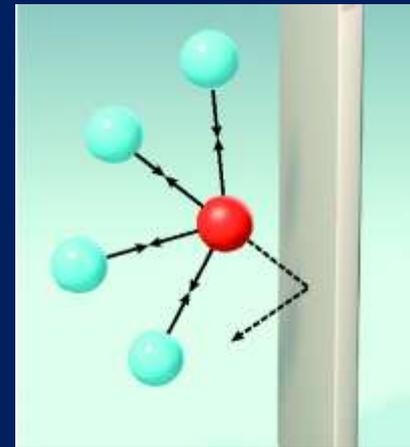
Graham's Law

- The rate of diffusion or effusion is inversely proportional to the square root of the *molar mass of particles.*

$$\frac{\text{Rate of diffusion/effusion for gas 1}}{\text{Rate of diffusion/effusion for gas 2}} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

11.7 Deviation from Ideal Behavior

- Real gases do not always behave ideally under certain conditions due to
 - Gas molecules occupy significant volume (at high pressures)
 - Gas molecules experience intermolecular forces of attraction and repulsion (at low temperatures)



Effect of intermolecular forces on P

- **Van der Waal's equation corrects for**
 - **Pressure deviations**

$$P_{\text{ideal}} = P_{\text{real}} + \frac{an^2}{V^2}$$

where *a* is a constant

- **Volume effects**

$$V_{\text{real}} = V_{\text{ideal}} - nb$$

where *b* is a constant

- The ideal gas law

$$PV = nRT$$

becomes van der Waal's equation

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

corrected
pressure term

corrected
volume term

***a* and *b* have specific values for each gas**

TABLE 11.6

Van der Waals Constants of Some Common Gases

Gas	$a \left(\frac{\text{atm} \cdot \text{L}^2}{\text{mol}^2} \right)$	$b \left(\frac{\text{L}}{\text{mol}} \right)$	Gas	$a \left(\frac{\text{atm} \cdot \text{L}^2}{\text{mol}^2} \right)$	$b \left(\frac{\text{L}}{\text{mol}} \right)$
He	0.034	0.0237	O ₂	1.36	0.0318
Ne	0.211	0.0171	Cl ₂	6.49	0.0562
Ar	1.34	0.0322	CO ₂	3.59	0.0427
Kr	2.32	0.0398	CH ₄	2.25	0.0428
Xe	4.19	0.0510	CCl ₄	20.4	0.138
H ₂	0.244	0.0266	NH ₃	4.17	0.0371
N ₂	1.39	0.0391	H ₂ O	5.46	0.0305

Key Points

- **Properties of gases**
 - **Gas pressure**
 - **Units**
 - **Calculation**
 - **Measurement**
- **The gas laws**
 - **Boyle's law**
 - **Charles' law**

Key Points

- Avogadro's law
- The ideal gas law
- Reactions with gaseous reactants and products
- Gas mixtures
 - Dalton's law
 - Mole fractions
 - Partial pressures

Key Points

- **The kinetic molecular theory**
 - Assumptions
 - Application to the gas laws
 - Molecular speed
 - Diffusion and effusion
- **Deviation from ideal behavior**
 - Factors causing deviation
 - Van der Waal's equation