

# Chapter 11



# Gases

# Properties of Gases

- Occupy the entire volume of their container
  - Compressible
  - Flow readily and mix easily
- Have low densities, low molecular weight

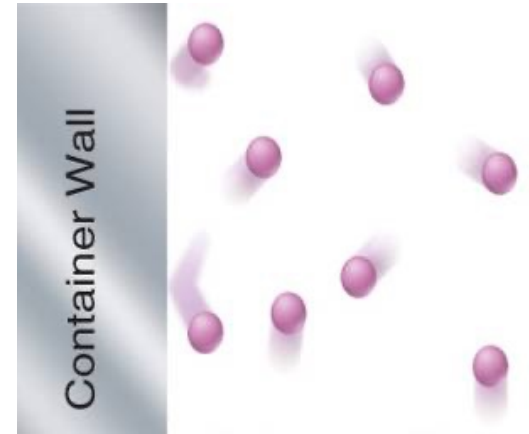
Some common gases:

Elements	Compounds
H <sub>2</sub> (molecular hydrogen)	HF (hydrogen fluoride)
N <sub>2</sub> (molecular nitrogen)	HCl (hydrogen chloride)
O <sub>2</sub> (molecular oxygen)	HBr (hydrogen bromide)
O <sub>3</sub> (ozone)	HI (hydrogen iodide)
F <sub>2</sub> (molecular fluorine)	CO (carbon monoxide)
Cl <sub>2</sub> (molecular chlorine)	CO <sub>2</sub> (carbon dioxide)
He (helium)	NH <sub>3</sub> (ammonia)
Ne (neon)	NO (nitric oxide)
Ar (argon)	NO <sub>2</sub> (nitrogen dioxide)
Kr (krypton)	N <sub>2</sub> O (nitrous oxide)
Xe (xenon)	SO <sub>2</sub> (sulfur dioxide)
Rn (radon)	H <sub>2</sub> S (hydrogen sulfide)

# Kinetic Molecular Theory

## Based on Some Assumptions:

- Molecules are in constant random motion
- There are large spaces between gas molecules
  - Molecules considered “volume-less”
  - Move easily when force is applied
  - No interaction between molecules
- Collisions are Elastic
  - Transfer but no gain or loss of energy
- Average kinetic energy is proportional to temp. in Kelvins
  - Molecules move faster as temp increases



## According to theory:

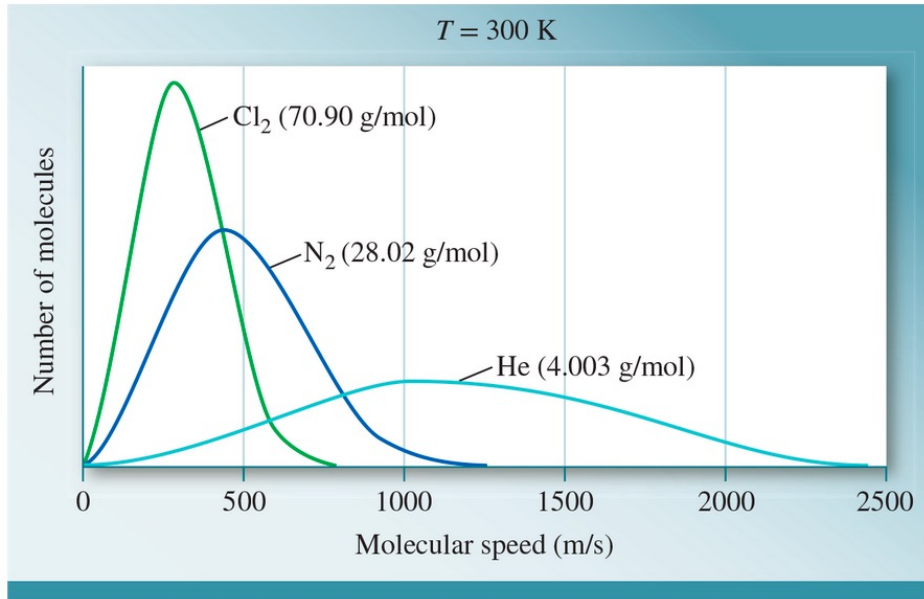
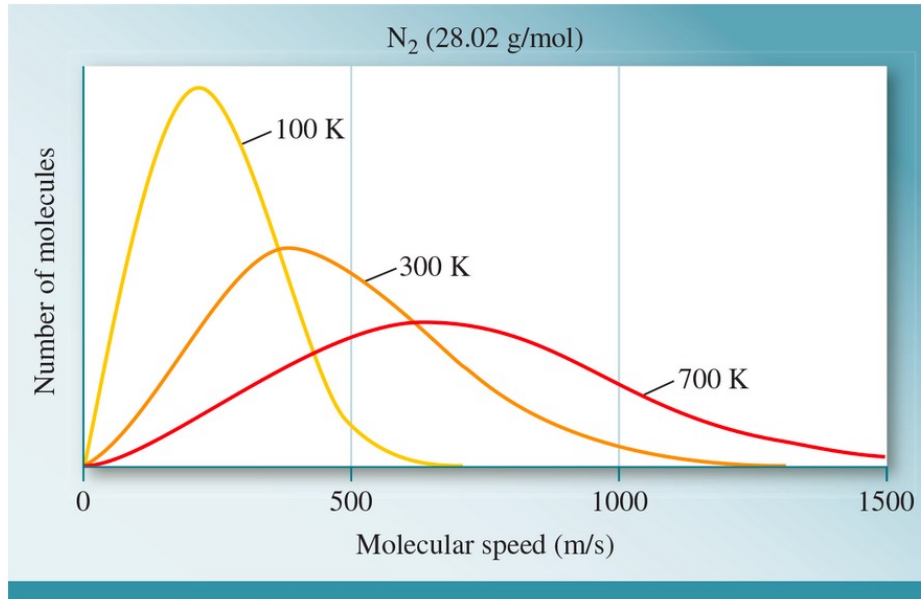
- Pressure is created by molecules hitting the walls
- Amount of pressure depends on frequency & strength of collisions

# Molar Mass & Temperature Effects: Root-Mean-Squared Speed

$$\sqrt{u_2} = u_{rms} = \sqrt{\frac{3RT}{MolarMass}}$$

At Higher temperatures  
molecules move faster

Small molecules move  
faster than big ones



# Calculation of $v_{rms}$

What is the  $v_{rms}$  of diatomic nitrogen at 20°C?

$$R = 8.314 \text{ J/mol K}$$

$$\sqrt{u_2} = u_{rms} = \sqrt{\frac{3RT}{MolarMass}}$$

$$A = 511 \text{ m/s}$$

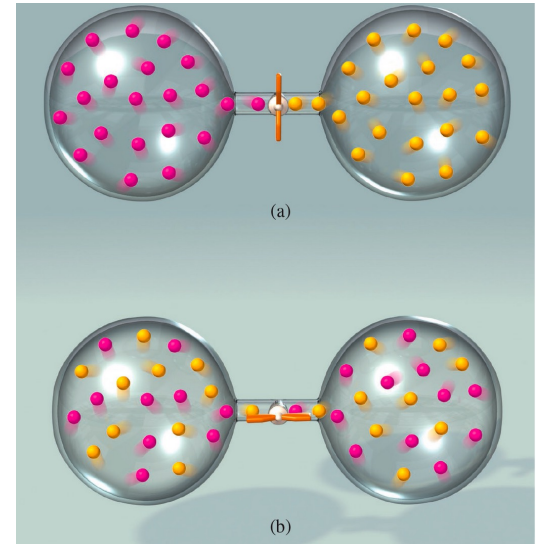
# Diffusion and Effusion

Diffusion is the process by which one gas mixes with another as a result of molecular movement

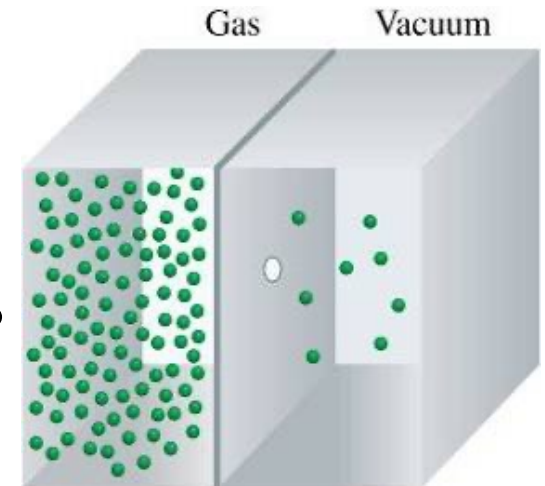


$$\text{Rate} \propto \frac{1}{\sqrt{M}}$$

NH<sub>4</sub>Cl collects closer to HCl  
 HCl molecules larger than NH<sub>3</sub> molecules



Effusion is the process in which a gas under pressure escapes from its container through a small hole.



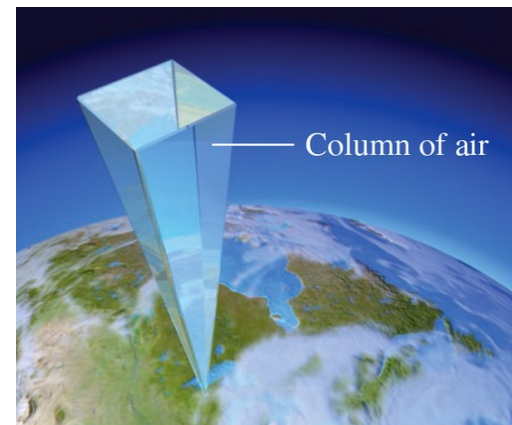
# Atmospheric Pressure

$$\text{Pressure} = \frac{\text{Force (N)}}{\text{Area (m}^2\text{)}}$$

Force = mass x acceleration  
= kg x m/s<sup>2</sup>

## Atmospheric pressure

- Pressure from earth's atmosphere at sea level
- Equal to ~ 1 atmosphere (atm)



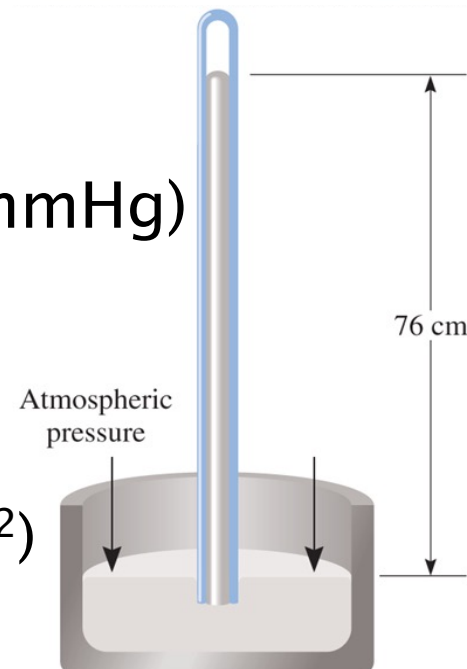
## Barometer

- Used to measure atmospheric pressure
- Measures height of Hg column in mm (mmHg)
- At sea level height is 760mm

In other pressure units: 1atm is equal to.....

760 mmHg      760 torr      101325 Pa (N/m<sup>2</sup>)

101.325 kPa      29.921 in. Hg      14.695 948 psi



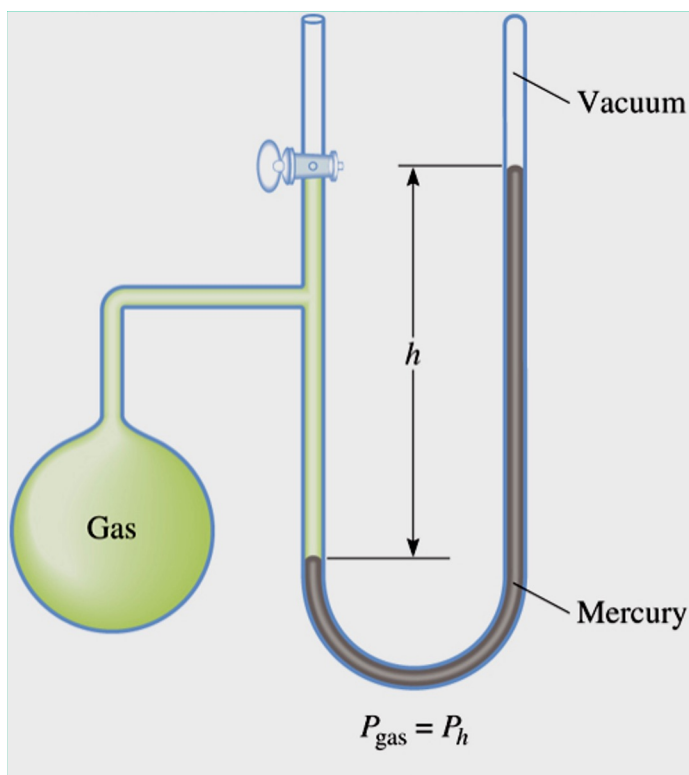
# Measuring Experimental Gas Pressure

A manometer measures pressure of gases

Closed tube manometer

Best for pressures  $< 1\text{atm}$

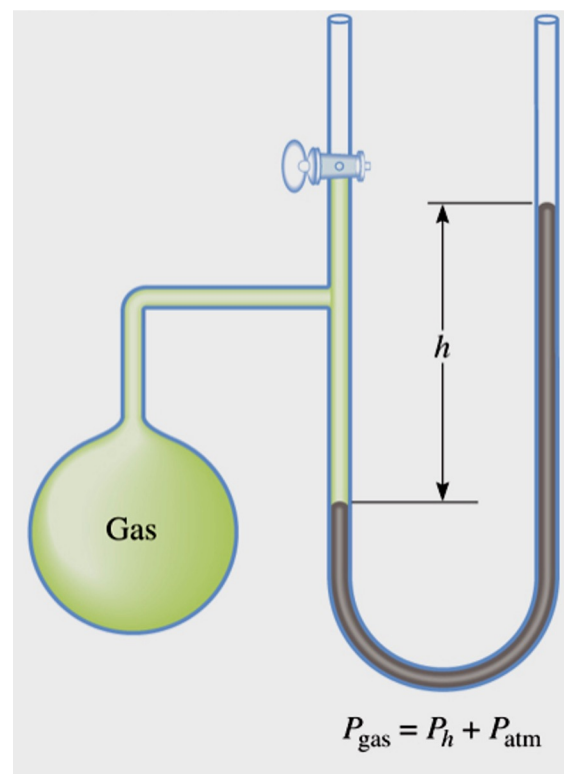
$$P_{\text{gas}} = \text{Height} = \text{mm Hg}$$



Open tube manometer

Best for pressures  $\geq 1\text{atm}$

$$P_{\text{gas}} = 760\text{mm Hg} + \text{height}$$



Use for Changing Conditions  
(have initial & final)

Use for Constant Conditions

$$PV = nRT$$

$$\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}$$

# Gas Laws

In case you should need them for HW:

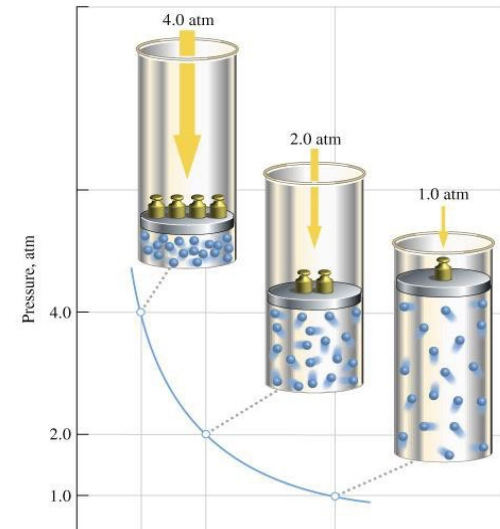
$$^{\circ}\text{C} = ( ^{\circ}\text{F} - 32 ) \times 5 / 9$$

$$^{\circ}\text{F} = ( ^{\circ}\text{C} \times 9 / 5 ) + 32$$

# Pressure/Volume Relationship

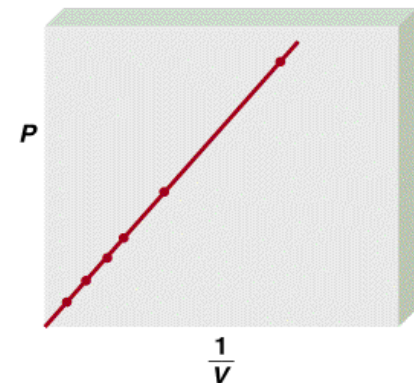
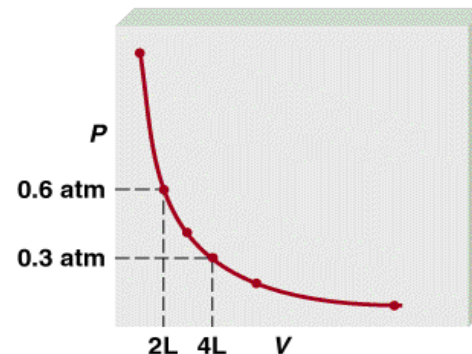
For a fixed amount of gas at constant temperature, volume decreases as pressure increases (**inverse relationship**)

$$PV = \text{constant so } P_1V_1 = P_2V_2$$



**↑ pressure: ↓ volume**  
Reduce space between molecules

**↓ volume: ↑ pressure**  
Increase molecule-wall collisions



# Volume/Temp. Relationship

For a fixed amount of gas at constant pressure, volume increases as temperature increases  
(direct relationship)

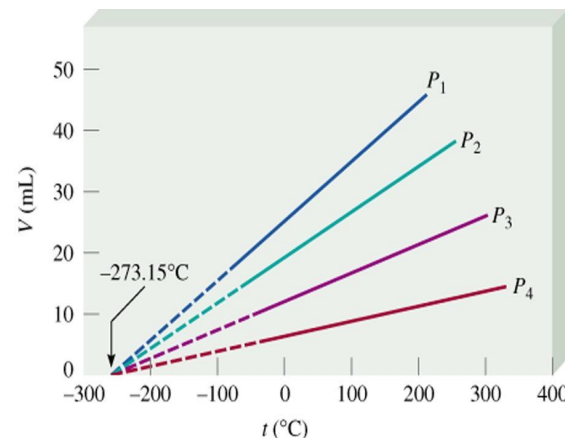
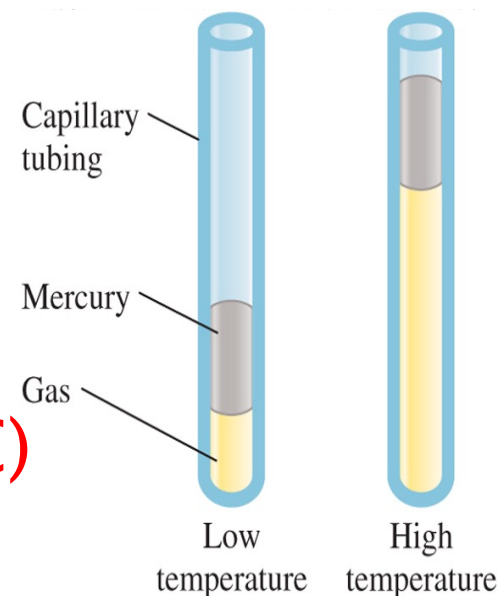
$$V/T = \text{constant so } V_1/T_1 = V_2/T_2$$

Temp. in **kelvins (K)**, not Celsius ( $^{\circ}\text{C}$ )

$$T (\text{K}) = ^{\circ}\text{C} + 273.15$$

As temperature increases:

- Molecules move faster
- They hit the wall harder
- Volume increases to hold pressure

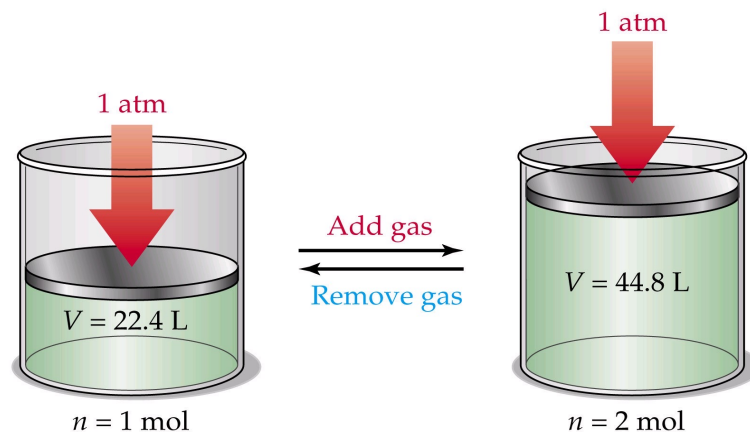


# Moles/Volume Relationship

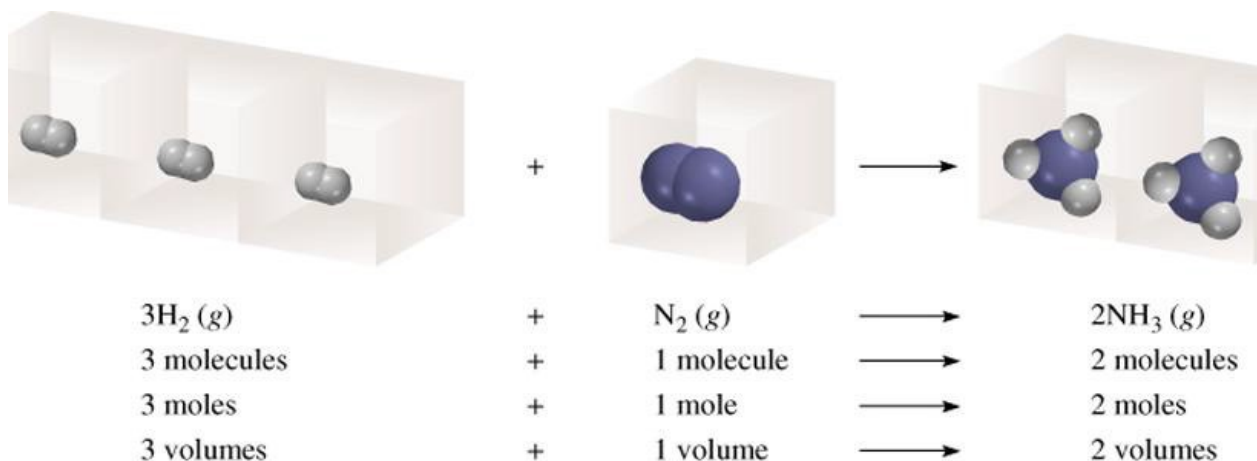
At fixed temperature and pressure, the volume of a gas depends on the # of moles of gas present

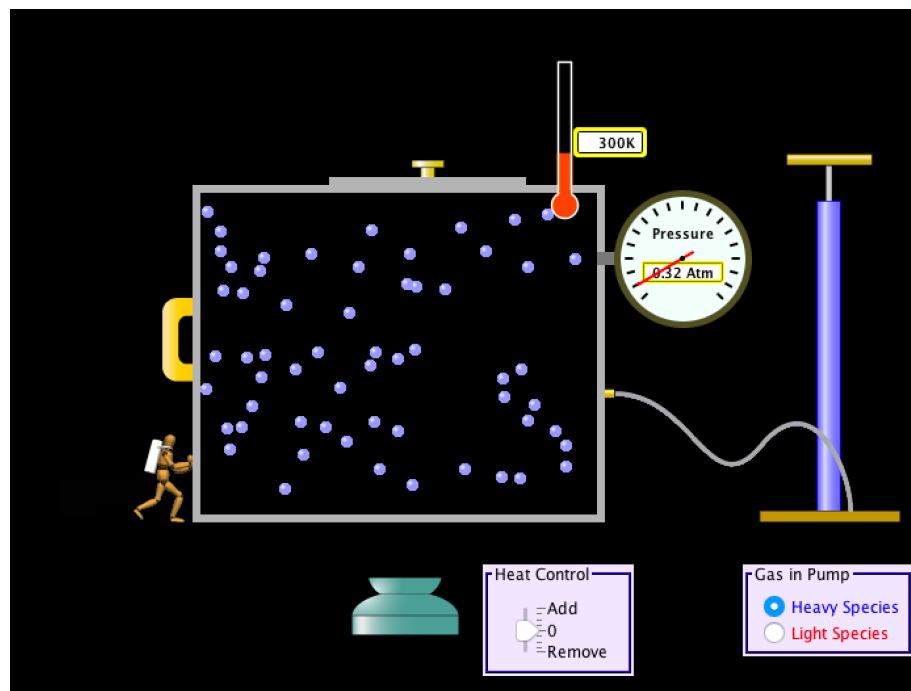
$V/n = \text{constant so}$

$$V_1/n_1 = V_2/n_2$$



More molecules need more space to maintain the same pressure and temperature





<https://phet.colorado.edu/en/simulation/legacy/gas-properties>

# The Combined Gas Law & the Ideal Gas Constant

## Combines all three laws

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

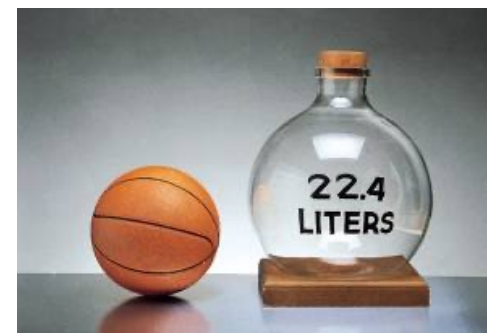
Standard Temperature and Pressure (STP) = 1atm & 273K  
At STP, 1 mole of gas occupies 22.4 L

$$\frac{P_1V_1}{n_1T_1} = \frac{1\text{atm} \times 22.4\text{L}}{1\text{mol} \times 273\text{K}} = \frac{0.0821\text{Latm}}{\text{molK}} = R$$

Ideal Gas Constant:  $R = \frac{0.0821\text{Latm}}{\text{molK}}$

Ideal Gas Law:

$$PV = nRT$$



# The Universal Gas Constant – $R$ – in alternative Units

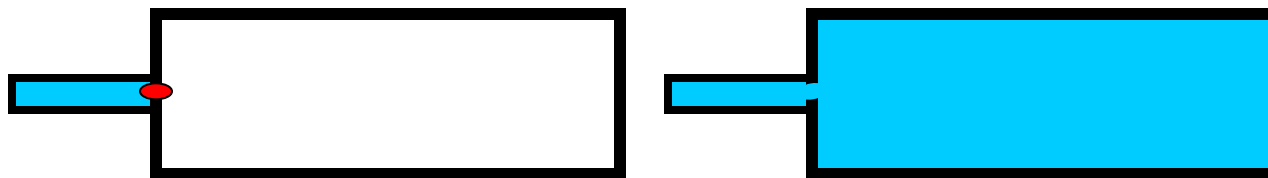
- $\text{atm} \cdot \text{cm}^3/(\text{mol} \cdot \text{K}) : 82.0575$
- $\text{atm} \cdot \text{ft}^3/(\text{lbmol} \cdot \text{K}) : 1.31443$
- $\text{atm} \cdot \text{ft}^3/(\text{lbmol} \cdot ^\circ\text{R}) : 0.73024$
- **$\text{atm} \cdot \text{l}/(\text{mol} \cdot \text{K}) : 0.08206$**
- $\text{bar} \cdot \text{cm}^3/(\text{mol} \cdot \text{K}) : 83.14472$
- $\text{bar} \cdot \text{l}/(\text{mol} \cdot \text{K}) : 0.08314472$
- $\text{Btu}/(\text{lbmol} \cdot ^\circ\text{R}) : 1.9859$
- $\text{cal}/(\text{mol} \cdot \text{K}) : 1.9859$
- $\text{erg}/(\text{mol} \cdot \text{K}) : 83144720$
- $\text{hp} \cdot \text{h}/(\text{lbmol} \cdot ^\circ\text{R}) : 0.0007805$
- $\text{inHg} \cdot \text{ft}^3/(\text{lbmol} \cdot ^\circ\text{R}) : 21.85$
- **$\text{J}/(\text{mol} \cdot \text{K}) : 8.314462$**
- $(\text{kgf}/\text{cm}^2) \cdot \text{l}/(\text{mol} \cdot \text{K}) : 0.084784$
- $\text{kPa} \cdot \text{cm}^3/(\text{mol} \cdot \text{K}) : 8314.472$
- $\text{kWh}/(\text{lbmol} \cdot ^\circ\text{R}) : 0.000582$
- $\text{lbf} \cdot \text{ft}/(\text{lbmol} \cdot ^\circ\text{R}) : 1545.349$
- $\text{mmHg} \cdot \text{ft}^3/(\text{lbmol} \cdot \text{K}) : 999$
- $\text{mmHg} \cdot \text{ft}^3/(\text{lbmol} \cdot ^\circ\text{R}) : 555$
- $\text{mmHg} \cdot \text{l}/(\text{mol} \cdot \text{K}) : 62.364$
- $\text{Pa} \cdot \text{m}^3/(\text{mol} \cdot \text{K}) : 8.314472$
- $\text{psf} \cdot \text{ft}^3/(\text{lbmol} \cdot ^\circ\text{R}) : 1545.349$
- $\text{psi} \cdot \text{ft}^3/(\text{lbmol} \cdot ^\circ\text{R}) : 10.73$
- $\text{Torr} \cdot \text{cm}^3/(\text{mol} \cdot \text{K}) : 62364$
- $\text{kJ}/(\text{kmol} \cdot \text{K}) : 8.314462$

**Units used in ideal gas equation must match  $R$  used**

A 4.50-L cylinder containing He(g) at an unknown pressure is connected to a 92.5-L evacuated cylinder. When the connecting valve between the two cylinders is opened, the pressure falls to 1.40 atm. What was the pressure in the 4.50-L cylinder?

Initial Conditions ( $P_1V_1$ )

Final Conditions ( $P_2V_2$ )



$$A = 30.2 \text{ atm}$$

A 16.4-g sample of a gas at 25.0 psi and 25.0°C is confined in a 17.5 L container. This gas is moved to a 28.5 L container at 100.0°C and 14.0 psi.

How much gas was removed or added?

**Changing conditions, so equation is:**

Note: Temperature must be converted to Kelvin, but since the units will cancel, the other units can be used as given.

**A = 4.5g removed**

Decreasing the temperature of 10.00 L of  $\text{H}_2$  (g) from  $25^\circ\text{C}$  to  $-77^\circ\text{C}$  decreases its volume to what value?

$$A = 6.58 \text{ L}$$

Sulfur hexafluoride ( $\text{SF}_6$ ) is a colorless and odorless gas.

Due to its lack of chemical reactivity, it is used as an insulator in electronic equipment. Calculate the pressure (in atm) exerted by 1.39 moles of the gas in a steel vessel of volume 6.09 L at  $55^\circ\text{C}$ .

$$A = 6.15 \text{ atm}$$

Identify the noble gas if 23.6 g exerts a pressure of 1293 torr at 37°C in a 17.5-L container.

A = Neon (20.2 g/mol)

**Using STP values for ideal gases as conversion factors:**

At STP (1 atm, 0°C) 1 mole of an ideal gas occupies 22.4 L

What is the Mass of 16.2 L of SF<sub>6</sub> at STP?

Can only use this relationship at STP!!!      A = 106 g

# Reality: The Van der Waal's Equation

- Most gases show deviations from ideal behavior.
- Assumptions of the kinetic-molecular theory not exact
  - At high pressure/density gases act more like liquids/solids
    - Attractive forces between molecules increase
    - Molecular volume no longer negligible

## Van der Waal's equation:

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

$a$  = Molecular attraction correction coefficient

- Ideal  $P$  is higher than the measured  $P$
- $P_{\text{actual}} = P + an^2/V^2$

$b$  = Volume correction coefficient

- Ideal  $V$  is lower than the container  $V$
- $V_{\text{actual}} = V - nb$

van der Waals  
Constants of Some  
Common Gases

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

**Larger & more polar = less ideal**

Carbon dioxide gas (1.00 mole) at 373 K occupies 536 mL & reads 50.0 atm pressure. What is the calculated pressure using:

(i) Ideal gas equation?

(ii) van der Waals equation?

Calculate the % deviation of each value from that observed.

van der Waals constants for CO<sub>2</sub>:  $a = 3.592 \text{ L}^2 \text{ atm mol}^{-2}$   
 $b = 0.04267 \text{ L mol}^{-1}$

**(i) Using the Ideal Gas Equation:  $PV = nRT$**

$$V = 0.536 \text{ L}$$

$$T = 373 \text{ K}$$

$$N = 1.00 \text{ mol}$$

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

$$P = nRT/V = [(1.00 \text{ mol})(0.0821 \text{ L atm/mol K})(373 \text{ K})]/0.536 \text{ L}$$

$$\mathbf{P = 57.1 \text{ atm}}$$

$$\% \text{ deviation} = [(50.0 \text{ atm} - 57.1 \text{ atm})/50.00 \text{ atm}] \times 100$$

$$\mathbf{\% \text{ deviation} = 14.2 \%}$$

## (ii) Using Van der Waals equation:

$$[P + a(n^2/V^2)][V - (nb)] = nRT$$

$$[P + 3.592 \times (1.00/0.536)^2][0.536 - (1.00 \times 0.04267)] = (1.00 \times 0.082057 \times 373)$$

$$(P + 12.5028)(0.49333) = 30.607261$$

$$P + 12.5028 = 62.04216$$

$$P = 49.5394 \text{ atm}$$

$$\% \text{ deviation} = [(50.0 - 49.5)/50] \times 100$$

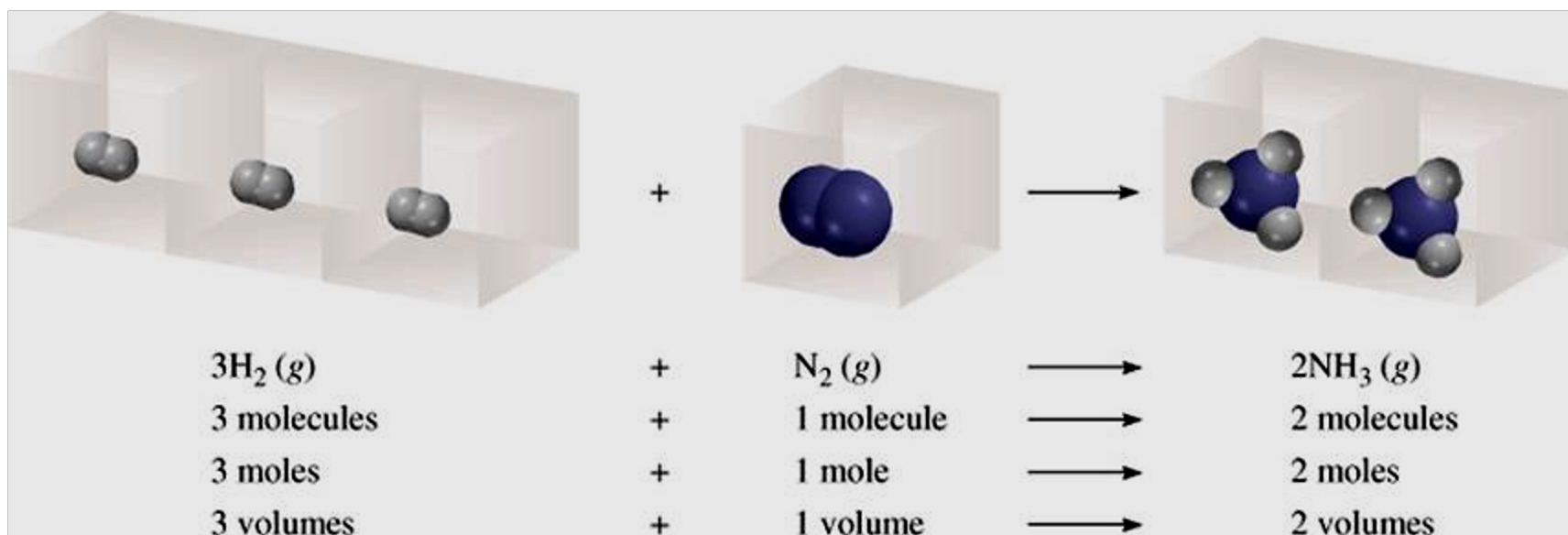
$$\% \text{ deviation} = 1.00\%$$

**Ideal: 14.2 % vs. van der Waals: 1.00%**

# The Law of Combining Volumes

At the same T and P, the volume of a gas is directly related to the moles of gas and the number of molecules of a gas.

The ratio is the same as that in the chemical equation



**Gases ONLY!**

Relationship requires there to be NO CHANGE in T & P

Ammonia burns in oxygen to form nitric oxide (NO) & water vapor. How many liters of water vapor are obtained from 2.0 liters of ammonia assuming there is no change in temperature and pressure?

Write the balanced chemical equation

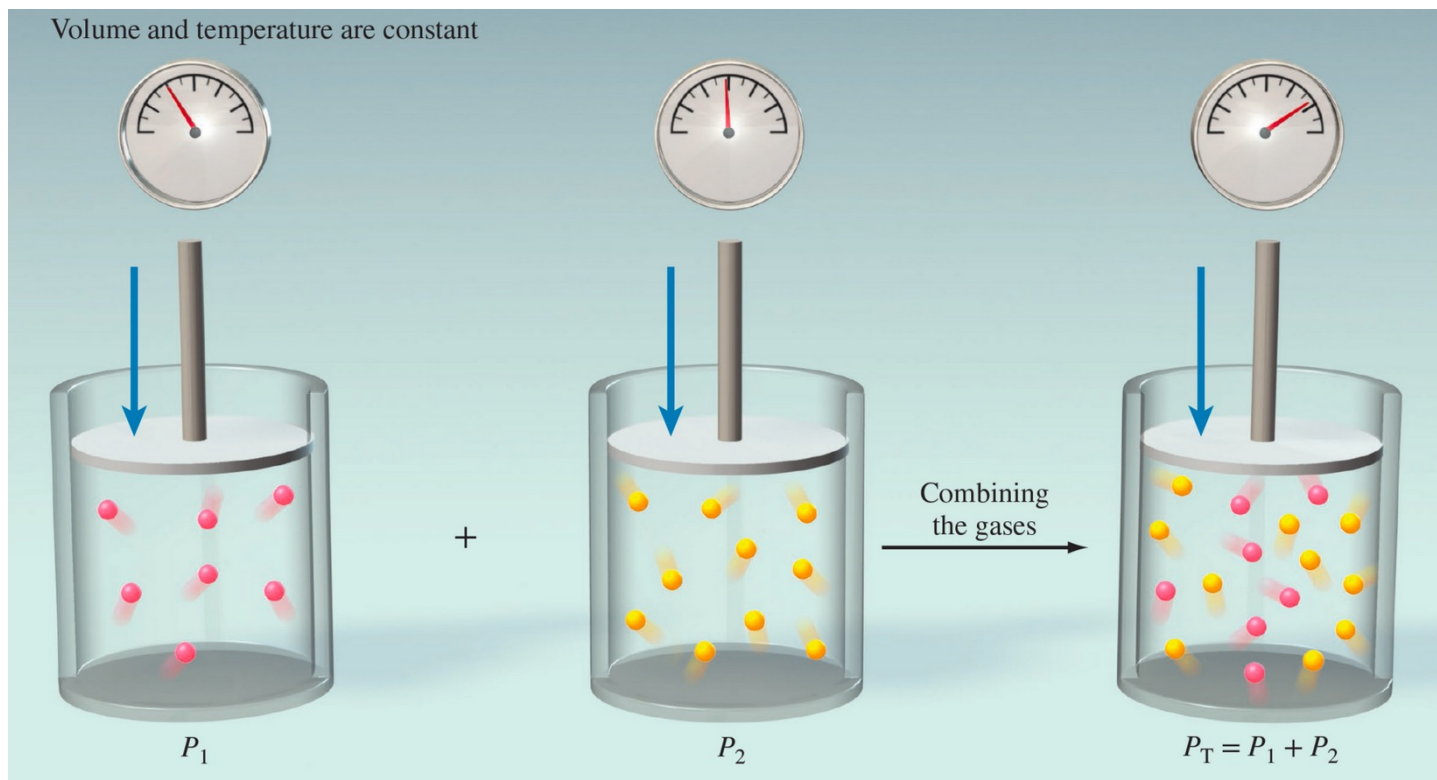


Get the volume ratio from the balanced equation

Use volume ratio to convert 2.0 liters of  $\text{NH}_3$  to vol.  $\text{H}_2\text{O}$

$$A = 3 \text{ L H}_2\text{O}$$

# Mixtures of Gases and Gas Stoichiometry



# Mixtures of Gases:

## Dalton's Law of Partial Pressures

Total Pressure = the sum of the partial pressures.

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

Partial Pressure = the pressure exerted by each individual gas in the container.

$$P_1 = (n_1RT)/V; \quad P_2 = (n_2RT)/V; \text{ etc.}$$

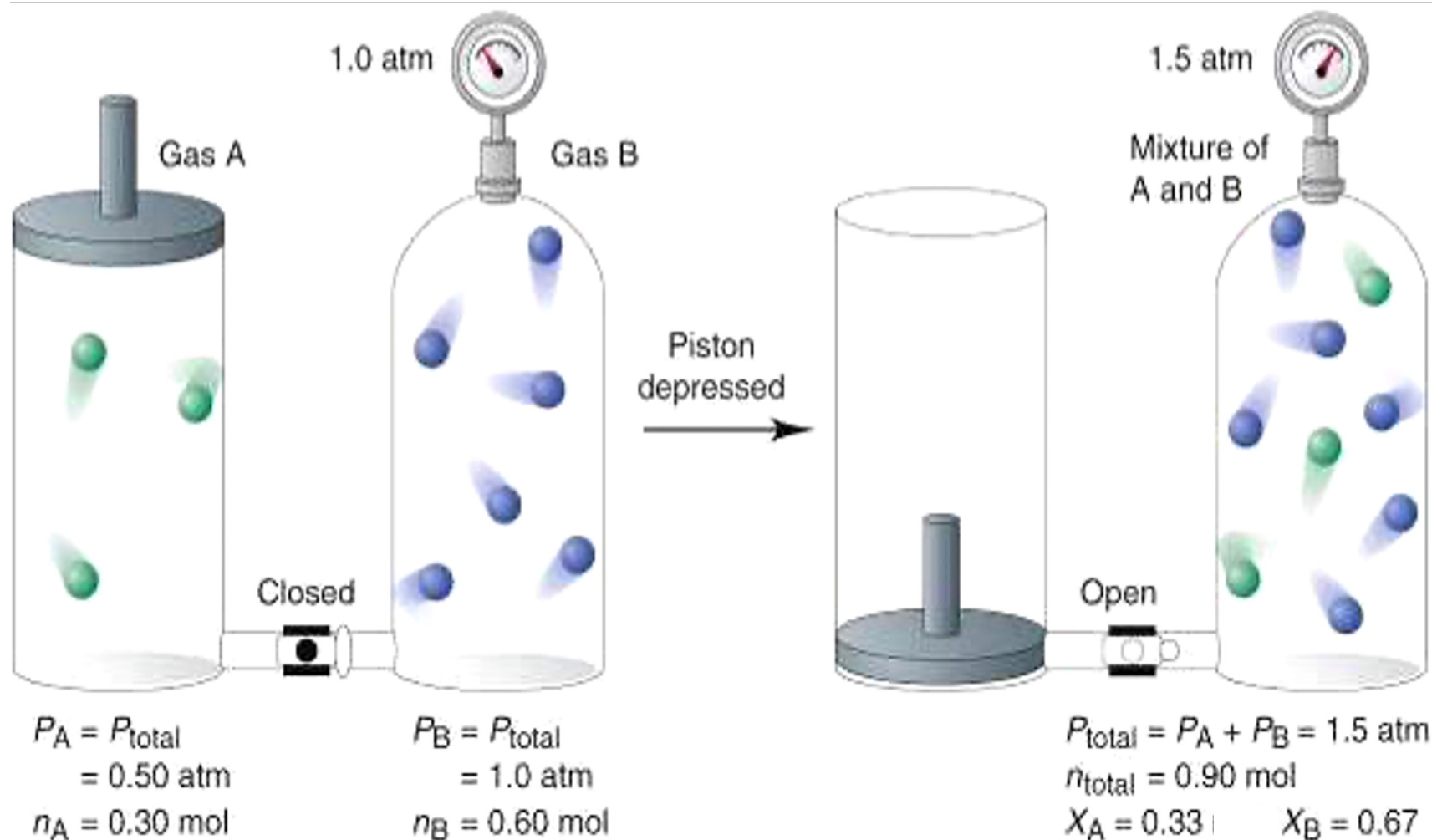
Mole Fraction = the moles of a given type of gas in a mixture divided by the total number of moles.

$$P_1/P_{\text{total}} = n_1/n_{\text{total}} = x_1$$

$$\text{Partial Pressure} = P_1 = x_1 \cdot P_{\text{total}}$$

# Mixtures of Gases

## Dalton's Law of Partial Pressures



A sample of natural gas contains 8.24 moles of  $\text{CH}_4$ , 0.421 moles of  $\text{C}_2\text{H}_6$ , and 0.116 moles of  $\text{C}_3\text{H}_8$ . If the total pressure of the gases is 1.37 atm, what is the partial pressure of propane ( $\text{C}_3\text{H}_8$ )?

$$A = 0.0181 \text{ atm}$$

# Collection of Gases Over Water

A gas is collected into a container of water

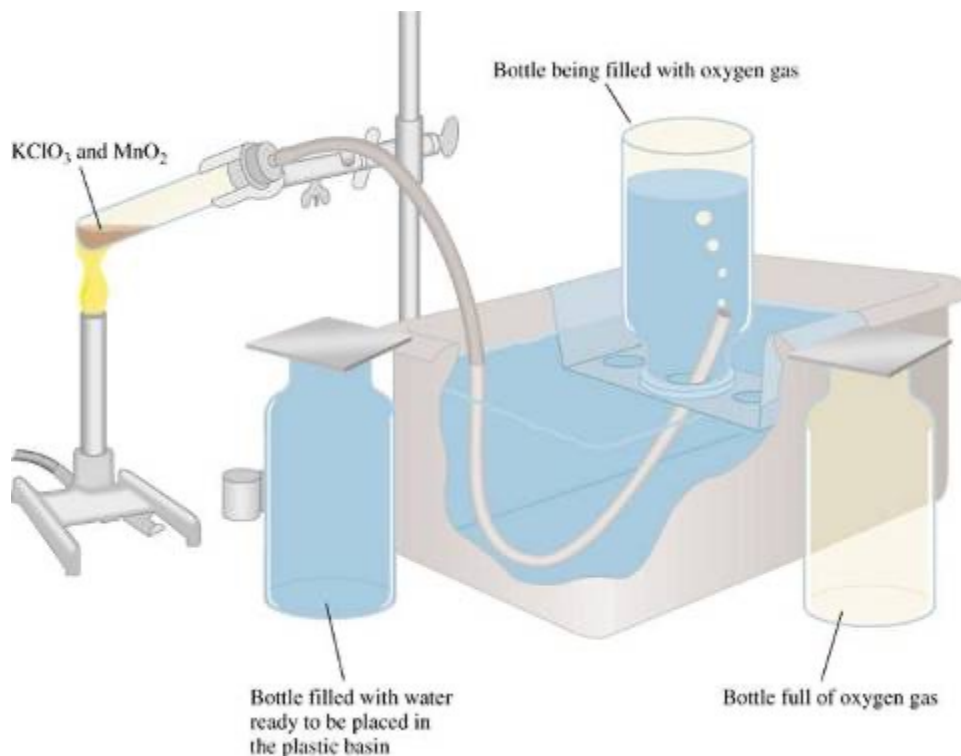
- Water saturated gas rises and displaces liquid water

Water is present in the gas phase above the liquid water

- The vapor pressure of the water must be subtracted from the measured pressure of the gas

$$P_{\text{total}} = P_{\text{atm}} = P_{\text{gas}} + P_{\text{water(g)}}$$

$$P_{\text{gas}} = P_{\text{atm}} - P_{\text{water(g)}}$$

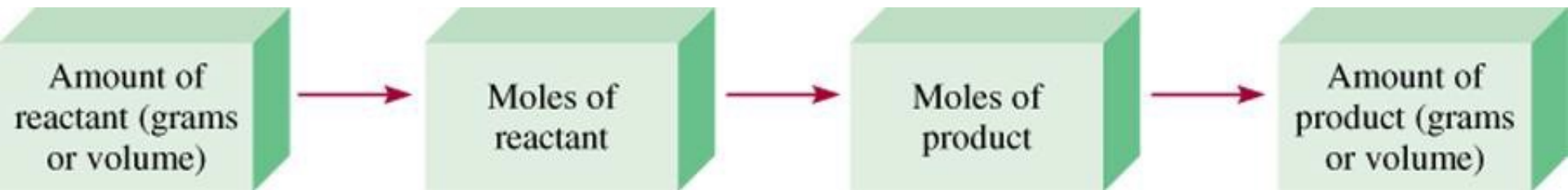


**TABLE 11.6**

Vapor Pressure of Water ( $P_{\text{H}_2\text{O}}$ ) as a Function of Temperature

$T$ (°C)	$P$ (torr)	$T$ (°C)	$P$ (torr)	$T$ (°C)	$P$ (torr)
0	4.6	35	42.2	70	233.7
5	6.5	40	55.3	75	289.1
10	9.2	45	71.9	80	355.1
15	12.8	50	92.5	85	433.6
20	17.5	55	118.0	90	525.8
25	23.8	60	149.4	95	633.9
30	31.8	65	187.5	100	760.0

# Gas Stoichiometry



What is the volume of  $\text{CO}_2$  produced at  $37^\circ\text{C}$  and  $1.00\text{ atm}$  when **5.60 g** of glucose ( $180.15768\text{g/mol}$ ) are used up in the Reaction?

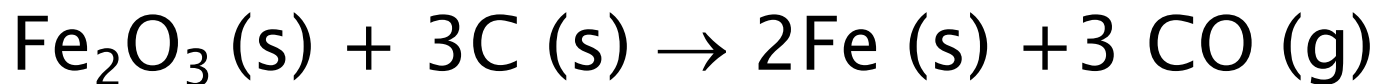


**A: 4.75 L**

## Additional Practice

### Stoichiometry and Gas Laws

What volume in liters of CO (g) at 250°C and 0.904 atm is produced from 453.6g Fe<sub>2</sub>O<sub>3</sub> (s) in the following reaction:



A: 405 L