## 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)		
O2 (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

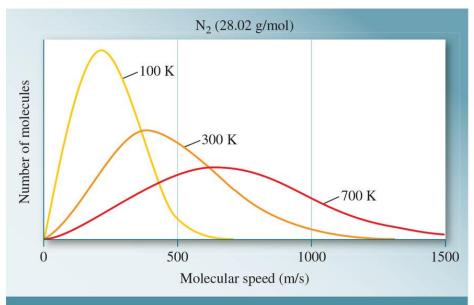


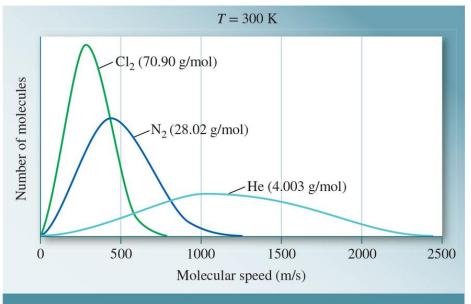
## Molar Mass & Temperature Effects: Root-Mean-Squared Speed

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

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?

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

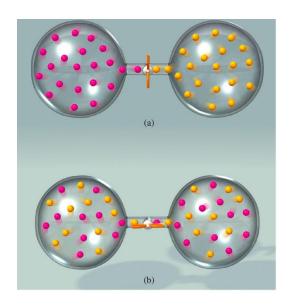
$$\sqrt{u_2} = u_{rms} = \sqrt{\frac{3RT}{MolarMass}}$$

## **Diffusion and Effusion**

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

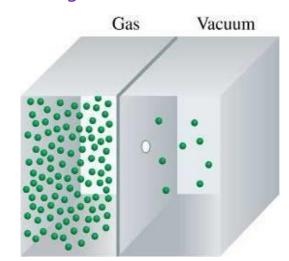


NH<sub>4</sub>CI



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.



Column of air

## **Atmospheric Pressure**

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

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

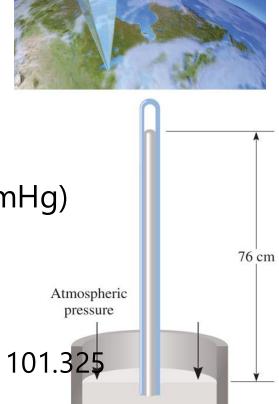
#### In other pressure units: 1atm is equal to.....

760 mmHg

760 torr

101325 Pa (N/m<sup>2</sup>) 101.325

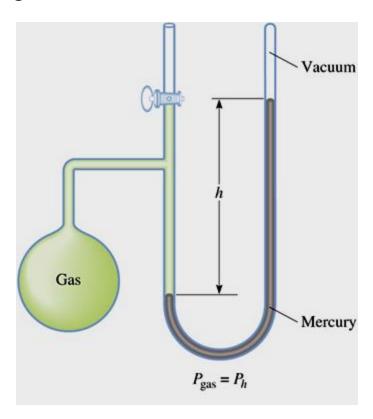
kPa 29.921 in. Hg 14.695 948 psi

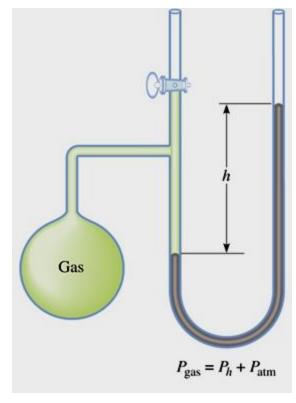


## **Measuring Experimental Gas Pressure**

### A manometer measures pressure of gases

Closed tube manometer Best for pressures <1atm  $P_{gas}$  = Height = mm Hg Open tube manometer
Best for pressures  $\geq 1$ atm  $P_{gas} = 760$ mm Hg + 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:

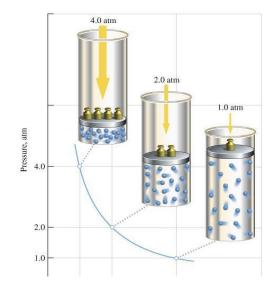
### **Pressure/Volume Relationship**

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

 $PV = constant so P_1V_1 = P_2V_2$ 

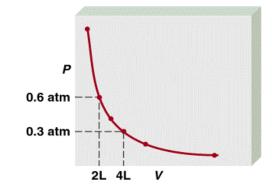
†pressure: \u00e4volume

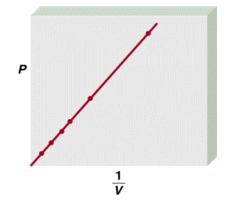
Reduce space between molecules



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)

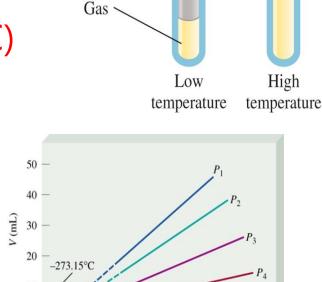
$$V/T=$$
 constant so  $V_1/T_1=V_2/T_2$ 

Temp. in **kelvins (K)**, not Celsius (°C)

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

### As temperature increases:

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



Capillary tubing

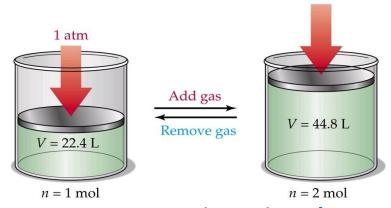
Mercury

1 atm

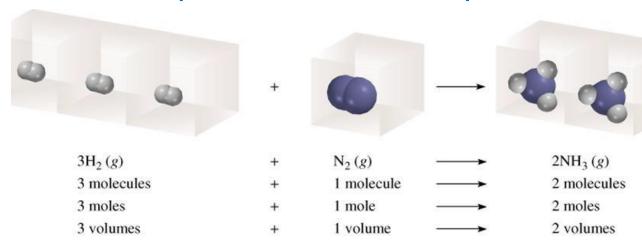
## **Moles/Volume Relationship**

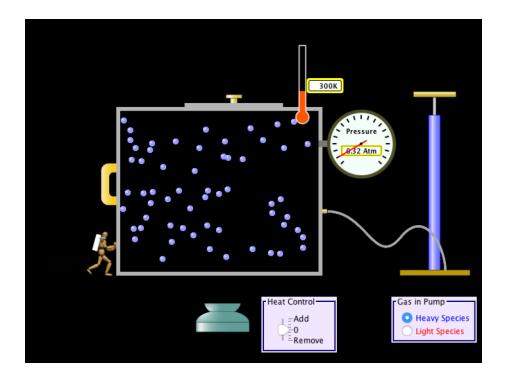
At fixed temperature and pressure, the volume of a gas depends on the # of moles of gas present

$$V/n = constant so$$
  
 $V_1/n_1 = V_2/n_2$ 



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**

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

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

$$\frac{P_1V_1}{n_1T_1} = \frac{1atmx22.4L}{1molx273K} = \frac{0.0821Latm}{molK} = R$$

Ideal Gas Constant: 
$$R = \frac{0.08206 Latm}{mol K}$$

Ideal Gas Law: PV = nRT

$$PV = nRT$$



#### The Universal Gas Constant - R - in alternative Units

```
atm · cm³/(mol · K) : 82.0575
atm · ft³/(lbmol · K) : 1.31443
atm · ft³/(lbmol · °R) : 0.73024
atm · l/(mol · K) : 0.08206
bar · cm³/(mol · K) : 83.14472
bar · l/(mol · K) : 0.08314472
Btu/(lbmol · °R) : 1.9859
cal/(mol · K) : 83144720
applies of t³/(lbmol · °R) : 0.0007805
in Hg · ft³/(lbmol · °R) : 21.85
```

■ J/(mol·K): 8.314462

```
• (kgf/cm<sup>2</sup>) • I/(mol • K) : 0.084784
• kPa · cm³/(mol.K) : 8314.472
• kWh/(lbmol • ∘R) : 0.000582
■ lbf • ft/(lbmol • °R) : 1545.349
■ mmHg • ft³/(lbmol • K) : 999
• mmHg • ft^3/(lbmol • ^{\circ}R) : 555
■ mmHg · I/(mol · K) : 62.364
■ Pa \cdot m^3/(mol \cdot K) : 8.314472
■ psf•ft³/(lbmol•°R) : 1545.349
■ psi·ft³/(lbmol·oR): 10.73
■ Torr·cm³/(mol·K): 62364
■ kJ/(kmol·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<sub>1</sub>V<sub>1</sub>) Final Conditions (P<sub>2</sub>V<sub>2</sub>)

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 H<sub>2</sub> (g) from 25°C to - 77°C decreases its volume to what value?

Sulfur hexafluoride (SF<sub>6</sub>) 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°C.

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

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

At STP (1 atm, O°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?

### 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:

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

- a = Molecular attraction correction coefficient
  - Ideal P is higher than the measured P
  - $P_{actual} = P + an^2/V^2$
- b = Volume correction coefficient
  - Ideal V is lower than the container V
  - V<sub>actual</sub>= V-nb

van der Waals Constants of Some Common Gases

	a	b
Gas (	$\frac{\text{atm} \cdot \text{L}^2}{\text{mol}^2}$	$\left(\frac{L}{\text{mol}}\right)$
Не	0.034	0.0237
Ne	0.211	0.0171
Ar	1.34	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0266
$H_2$	0.244	0.0266
N <sub>2</sub>	1.39	0.0391
$O_2$	1.36	0.0318
$Cl_2$	6.49	0.0562
$CO_2$	3.59	0.0427
CH <sub>4</sub>	2.25	0.0428
CCI <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  $CO_2$ :  $a = 3.592 L^2$  atm mol<sup>-2</sup>  $b = 0.04267 L mol^{-1}$ 

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

V = 0.536 L

T = 373 K

N = 1.00 mol R = 0.0821 L atm / mol K

P = nRT/V = [(1.00 mol)(0.0821 L atm/mol K)(373 K)]/0.536 LP = 57.1 atm

% deviation =  $[(50.0 \text{ atm} - 57.1 \text{ atm})/50.00 \text{ atm}] \times 100$ % deviation = 14.2 %

#### (ii) Using Van der Waals equation:

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

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

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

$$P + 12.5028 = 62.04216$$

$$P = 49.5394$$
 atm

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

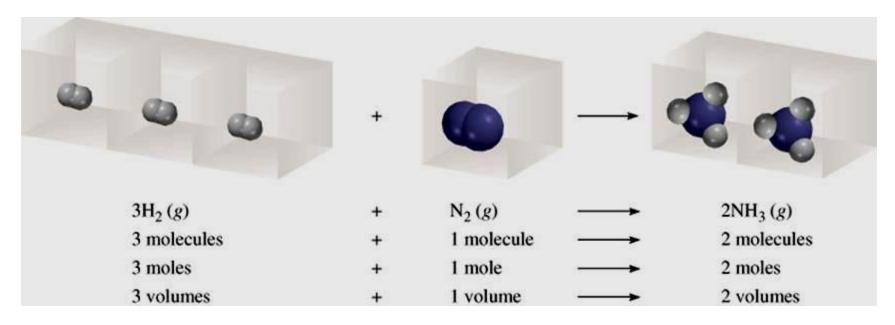
**% deviation = 1.00%** 

**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?

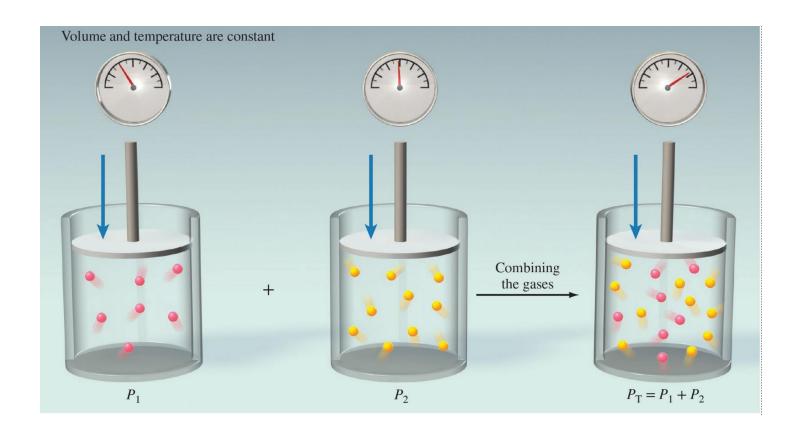
#### Write the balanced chemical equation

$$4 \text{ NH}_3 (g) + 5 \text{ O}_2 (g) \rightarrow 4 \text{ NO } (g) + 6 \text{ H}_2 \text{O } (g)$$

Get the volume ratio from the balanced equation

Use volume ratio to convert 2.0 liters of NH<sub>3</sub> to vol. H<sub>2</sub>O

# Mixtures of Gases and Gas Stoichiometry



## Mixtures of Gases: Dalton's Law of Partial Pressures

<u>Total Pressure</u> = the sum of the partial pressures.

$$P_{total} = P_1 + P_2 + P_3 + \cdots$$

<u>Partial Pressure</u> = the pressure exerted by each individual gas in the container.

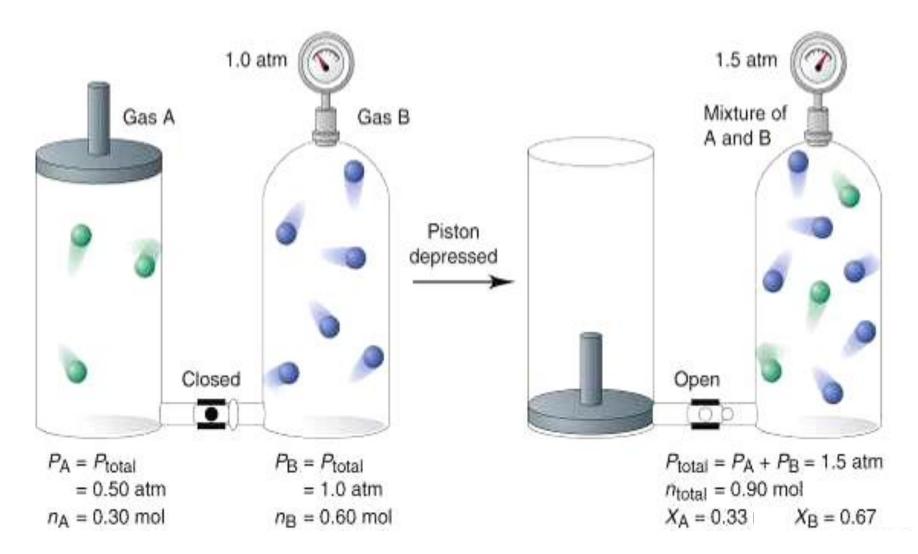
$$P_1 = (n_1RT)/V$$
;  $P_2 = (n_2RT)/V$ ; etc.

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

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

Partial Pressure = 
$$P_1 = X_1 \cdot P_{total}$$

# Mixtures of Gases Dalton's Law of Partial Pressures



A sample of natural gas contains 8.24 moles of  $CH_4$ , 0.421 moles of  $C_2H_6$ , and 0.116 moles of  $C_3H_8$ . If the total pressure of the gases is 1.37 atm, what is the partial pressure of propane  $(C_3H_8)$ ?

#### **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

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

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

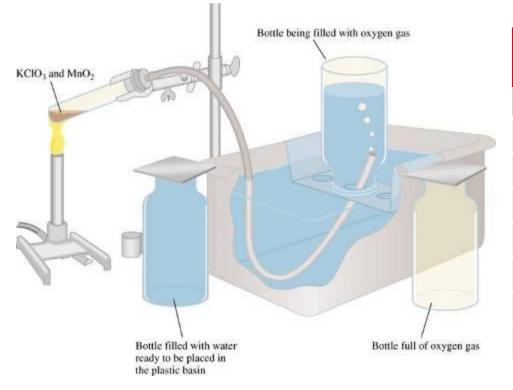
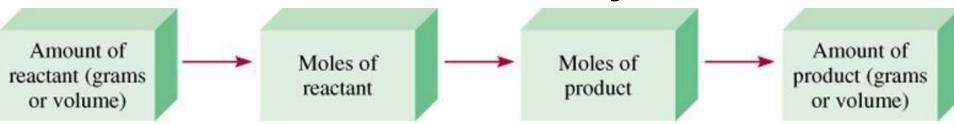


TABLE 1		Vapor Pressure of Water $\left(P_{\mathrm{H_2O}}\right)$ as a Function of Temperature					
<b>T</b> (°C)	P (torr)	<b>T</b> (°C)	P (torr)	T (°C)	P (torr)		
0	4.6	35	42.2	70	233.7		
5	6.5	40	55.3	75	289.1		
10	9.2	45	71.9	80	355.1		
15	12.8	50	92.5	85	433.6		
20	17.5	55	118.0	90	525.8		
25	23.8	60	149.4	95	633.9		
30	31.8	65	187.5	100	760.0		

**Gas Stoichiometry** 



What is the volume of CO<sub>2</sub> produced at 37°C and 1.00 atm when 5.60 g of glucose (180.15768g/mol) are used up in the Reaction?

$$C_6H_{12}O_6$$
 (s) +  $6O_2$  (g)  $\longrightarrow$   $6CO_2$  (g) +  $6H_2O$  (l)  
g  $C_6H_{12}O_6$   $\longrightarrow$  mol  $C_6H_{12}O_6$   $\longrightarrow$  mol  $C_6H_{12}O_6$   $\longrightarrow$   $O_2$ 

#### **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:

$$Fe_2O_3(s) + 3C(s) \rightarrow 2Fe(s) + 3CO(g)$$