Chapter 5
Gases

Read/Study: Chapter 5

Memorize: *Nothing!*

MGC Assignments: *See MGC Website!*

The Nature of Gases

An Introduction to the States of Matter

Byron K. Christmas, Ph.D.

Concept:

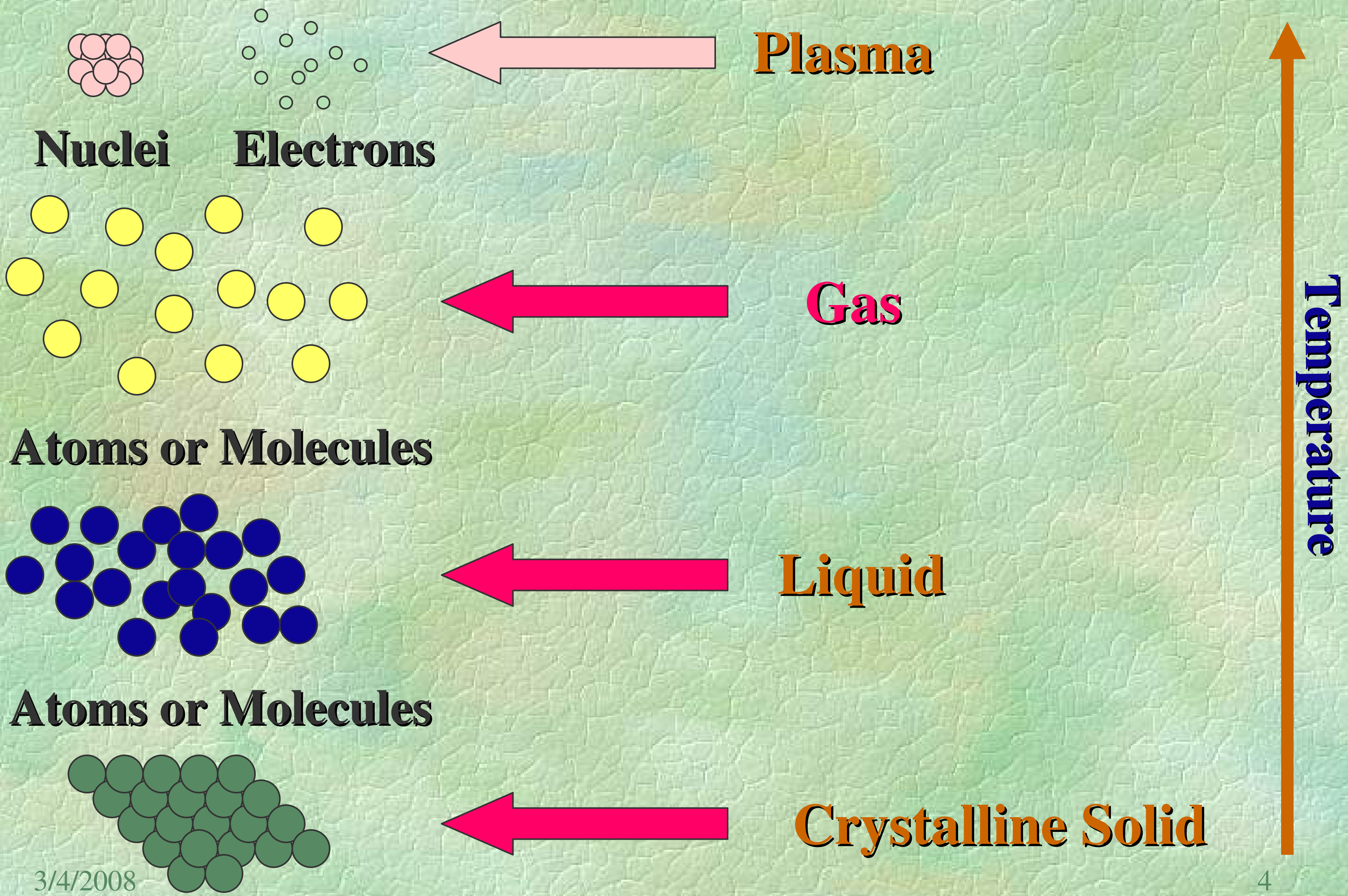
What could you do to change a crystalline solid to a liquid and then a gas and then a plasma?

1. ***Raise the temperature***

2. ***Raise the atmospheric pressure***

3. ***Lower the atmospheric pressure***

1. Introduction: The States of Matter



A. The Solid State

- **Solids retain their shape regardless of the shape of their container.**
- **They retain their volume regardless of the size of their container.**
- **They are essentially *Incompressible*.**
- **They do NOT diffuse readily.**
- **Crystalline solids have a high degree of structure and order at the molecular level. Amorphous solids do not.**
- **They exhibit isotropic behavior.**

Concept:

Which of the following gives examples of both a crystalline solid <u>and</u> an amorphous solid?

1. ***Salt and sugar***
2. ***Iron and rubber band***
3. ***Glass bottle and plastic Coke® bottle***

B. The Liquid State

- Liquids are relatively rare in nature:

H_2O Br_2 Hg Lava

- They take the shape of their container.
- They retain their volume regardless of the size of the container.
- They are essentially incompressible.
- They diffuse relatively slowly.
- They exhibit surface tension and viscosity.
- They have very limited structure at the molecular level and exhibit isotropic behavior.

C. The Gaseous State - *General Properties*

- Gases take the shape of their container.
- They completely fill any container they are in.
- They are highly *compressible*.
- They diffuse rapidly.
- Their atoms, ions, or molecules are randomly distributed - they have no structure at the molecular level.
- They exhibit isotropic behavior.

D. The Gaseous State - *A Model*

"Ideal" Gases:

- Atoms and molecules of an 'ideal' gas have ***no*** volume.
- There are ***no*** interatomic or intermolecular attractive forces.
- They follow the Ideal Gas Law: $PV = nRT$
- All ideal gases are identical in most physical properties, i.e., their properties are independent of the nature of the gas.

Concept:

If one mole of H_2 molecules fills a container of 22.4 L volume and each atom of hydrogen has a radius of 1×10^{-8} cm, what percentage of the container will be filled by the molecules themselves?

1. ***2 %***
2. ***0.2%***
3. ***0.02%***

99.98 % of the container is empty!

Real Gases:

- Atoms and molecules **HAVE** a finite volume but it is only a small fraction of the volume of the container.
- Atoms and molecules **DO** attract one another though not to a very large extent.
- Real gases do show differences in most of their **physical** properties but only very slightly.

E. Summary - *Gases vs. Liquids & Solids*

- Atoms, ions, and molecules are much closer together in liquids and solids than they are in gases.
- Atoms, ions, and molecules in liquids and solids are moving at a much slower speed than they would be for the same material in the gaseous state.
- The slower speed (lower average kinetic energy) allows for higher intermolecular attractive forces. This means that the physical properties of liquids and solids are heavily dependent on the nature of material.

2. Measuring Volume, Temperature, and Pressure

A. Volume - ***Review the Chapter on Measurements***

$$1\ L = 1000\ mL = 1000\ cm^3 = 1000\ cc$$

B. Temperature - ***Review the Chapter on Measurements***

$$K = {}^{o}C + 273.15 \qquad {}^{o}F = (9/5)({}^{o}C) + 32$$

C. Pressure - A force that is exerted over a specified area.

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} = \frac{\text{Mass x Acceleration}}{\text{Area}}$$

$$\frac{\text{SI unit of force}}{\text{SI unit of area}} = \frac{kg \times (m/s^2)}{m^2} = \frac{\text{Newton}}{m^2}$$

$$\frac{\text{Newton}}{m^2} = \frac{kg}{m \cdot s^2} = \textit{Pascal}$$ (SI unit of Pressure)

Class Problem: ***A person weighing 208 lbs was wearing shoes that had square heels that measured 2.5 in. x 3.0 in. each. If this person stood on only one shoe AND only on the heel of that one shoe, how much pressure would he/she exert on the floor?***

$$P = \frac{\text{Force}}{\text{Area}} = \frac{208\ lb}{7.5\ in^2} = 28\ lb/in^2$$

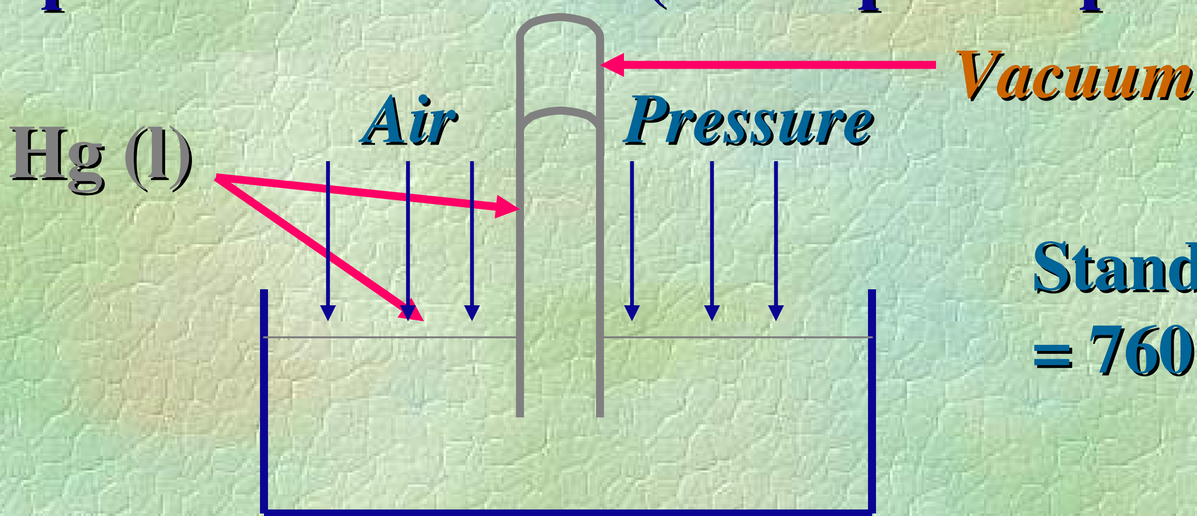
What if he/she changed shoes to one with a heel that measured 0.50 in. x 0.50 in.?

Area = 0.50 in x 0.50 in = 0.25 in^2

$$P = \frac{208\ lb}{0.25\ in^2} = 832\ lb/in^2$$

Fluids (Gases and Liquids) exert pressure in ALL directions. This allows us to measure their pressure.

Barometer **- An instrument used to measure the pressure of the air (atmospheric pressure).**



Standard Pressure = 760 mmHg

The height of the column of mercury above the surface of the liquid is a measure of the atmospheric pressure.

760 mmHg = 760 torr = 1 atmosphere

Class Problem: ***What is the barometric pressure in inches of mercury (inHg) if the barometer is reading 760.0 mmHg?***

$$\frac{(760.0\ \text{mmHg})}{} \frac{(1\ \text{cmHg})}{(10\ \text{mmHg})} \frac{(1\ \text{inHg})}{(2.540\ \text{cmHg})} = 29.90\ \text{inHg}$$

Class Problem: ***What is this barometric pressure in pascals?***

$$\frac{(760.0\ \text{mmHg})}{} \left| \frac{(1\ \text{mHg})}{(10^3\ \text{mmHg})} \right| \frac{(13.53\ \text{g Hg})}{(\text{cm}^3\ \text{Hg})} \left| \frac{(1\ \text{kg})}{(10^3\ \text{g})} \right| \frac{(10^2\text{cmHg})^3}{(\text{m Hg})^3}$$

$$= (1.028 \times 10^4\ \text{kg/m}^2)\ (9.80\ \text{m/s}^2) = 1.01 \times 10^5\ \text{Pa}$$

Concept:

A 1.0-L sample of an ideal gas is held in a container under 1.0 atm of pressure and at 25.3^{o}C. If the pressure on the container is raised to 2.0 atm, what will happen to the volume of the gas?

1. ***Decrease by 50%***

2. ***Increase by 100%***

3. ***Stay the Same***

Boyle's Law: **The volume of a gas is inversely proportional to the pressure when the temperature and amount of gas are held constant.**

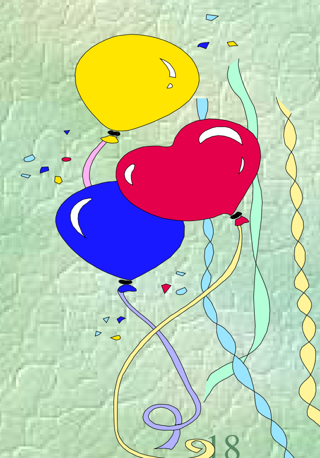
$V \propto 1/P$ **At constant T and n**

$V = k_1/P$ $PV = k_1 = \text{constant}$

$P_1V_1 = P_2V_2 = P_3V_3 = k_1$

The value of k_1 is dependent upon the temperature and the amount of gas present (number of moles).

You can use your "imaginary" balloon to do calculations.



Class Problem: ***A sample of a gas at constant temperature has a volume of 325 mL at a pressure of 538 mmHg. What will be its volume if the pressure is changed to 274 mmHg?***

	Volume, mL	Pressure, mmHg
Initial	325	538
Final	??	274

The pressure is decreasing so the volume will **INCREASE**.

$$(325\ \text{mL})\ \frac{(538\ \text{mm}\cancel{\text{Hg}})}{(274\ \text{mm}\cancel{\text{Hg}})} = 638\ \text{mL}$$

Concept:

A 1.0-L sample of an ideal gas is held in a container under 1.0 atm of pressure and at 300 K. If the temperature of the gas is raised to 450 K, what will happen to the volume of the gas?

1. ***Increase by 50%***
2. ***Decrease by 50%***
3. ***Stay the Same***

Charles' Law: **The volume of a gas is directly proportional to the absolute (Kelvin) temperature when the pressure and amount of gas are held both held constant.**

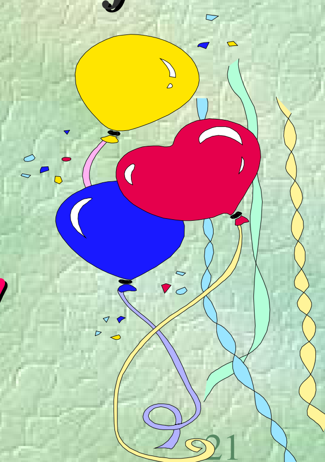
$V \ \alpha \ T$ **Constant p and n**

$V = k_2T$ $V/T = k_2 = \text{constant}$

$V_1T_1 = V_2T_2 = V_3T_3 = k_2$

k_2 is dependent upon the pressure and the amount of gas present (number of moles).

Hello….Don't forget to use your "imaginary" balloons for calculations!!



Kelvin Temperature Scale: **A temperature scale based on the Celsius temperature scale and a concept of absolute zero.**

$$K = (t^{o}C + 273.15^{o}C)(1\ K/1^{o}C) = T\ K$$

$$(-15^{o}C + 273.15^{o}C)(1\ K/1^{o}C) = 258\ K$$

Does Charles' Law work using the Celsius temperature scale?

Volume	25.0 mL	28.6 mL	32.4 mL
^{o}C	0.0	40.0	80.0
K	273.2	313.2	353.2

$$V/T = k_2 = \text{constant}$$

V/^{o}C = 25.0 mL/0.0^{o}C = undefined (∞)

28.6 mL/40.0^{o}C = 0.715 mL/^{o}C

32.4 mL/80.0^{o}C = 0.405 mL/^{o}C

∴ V/^{o}C ≠ constant!

V/K = 25.0 mL/273.2 K = 0.0915 mL/K

28.6 mL/313.2 K = 0.0913 mL/K

32.4 mL/353.2 K = 0.0917 mL/K

∴ V/K = constant ***(within 0.219 %)***

Class Problem: ***A sample of a gas has a volume of 3.7 L at 40.0^{o}C. What will be the volume if the temperature is changed to 0.0^{o}C at constant pressure?***

	Volume, L	Temp., ^{o}C	Temp., K
Initial	3.7	40.0	313.2
Final	??	0.0	273.2

(40.0^{o}C + 273.2^{o}C)(1 K/1^{o}C) = 313.2 K

(0.0^{o}C + 273.2^{o}C)(1 K/1^{o}C) = 273.2 K

The temperature is decreasing so the volume will **DECREASE**.

$$(3.7\ L)\frac{(273.2\ \cancel{K})}{(313.2\ \cancel{K})} = 3.2\ L$$

Avogadro's Law: **The volume of a gas is directly proportional to the amount of gas (moles) in the sample when the pressure and temperature are held both held constant.**

$V \propto n$ **Constant P and T**

$V = k_3 n$ **$V/n = k_3 = \text{constant}$**

$V_1/n_1 = V_2/n_2 = V_3/n_3 = k_3$

k_3 is dependent upon the pressure and the temperature.

***Hello*….. What happens when we change all three variables at the same time??**

Concept:

If both the temperature of an ideal gas and its pressure are raised, what will be the effect on the volume?

1. ***Increase***
2. ***Decrease***
3. ***Depends on both the temperature and the pressure changes.***

Class Problem: ***A sample of a gas has a volume of 5.6 L at 25.0°C and 755 mmHg. What will be the volume at STP?***

	Volume, L	Press, torr	Temp., °C	Temp., K
Initial	5.6	755	25.0	*298.2*
Final	??	760	0.0	*273.2*

(5.6 L)(755 ~~torr~~/760 ~~torr~~)(273.2 ~~K~~)/(298.2 ~~K~~)

= 5.1 L

Ideal Gas Law: **The volume of a gas is directly proportional to the Kelvin temperature and the amount of gas (moles) and inversely proportional to the pressure.**

$$V = (k_1/P)k_2Tk_3n = \frac{k_1k_2k_3nT}{P}$$

$k_1k_2k_3$ = constant = **R** *(The Universal Gas Constant)*

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

$$PV = nRT$$

Hello…..*could you please tell me how I could find out the value of R?*

PV = nRT **R = (PV)/(nT)**

Let P = 1 atm, n = 1 mol, T = 273 K, and V = 22.4 L

then $$R = \frac{(1\ \text{atm})(22.4\ \text{L})}{(1\ \text{mol})(273\ \text{K})} = 0.0821\ \frac{(\text{L-atm})}{(\text{mol-K})}$$

Let P = 760 mmHg, n = 1 mol, T = 273 K, and V = 22.4 L

then $$R = \frac{(760\ \text{mmHg})(22.4\ \text{L})}{(1\ \text{mol})(273\ \text{K})} = 62.36\ \frac{(\text{mmHg-L})}{(\text{mol-K})}$$

Let P = 1520 torr, n = 1 mol, T = 546 K, and V = 22.4 L

then $$R = \frac{(1520\ \text{torr})(22.4\ \text{L})}{(1\ \text{mol})(546\ \text{K})} = 62.36\ \frac{(\text{torr-L})}{(\text{mol-K})}$$

Boyle's, Charles', and Avogadro's Laws are all Special Cases of the Ideal Gas Law:

Boyle's Law -

$PV = nRT = k_1$ when n and T are constant.

Charles' Law -

$V/T = (nR)/P = k_2$ when n and P are constant.

Avogadro's Law -

$V/n = (RT)/P = k_3$ when T and P are constant.

Class Problem: ***What is the volume of 1.0 mol of N_2 (g) at STP? What about H_2 (g)?***

PV = nRT **V = nRT/P**

$$V = \frac{(1.0\ \text{mol})(0.0821\ \text{L-atm-mol}^{-1}\text{-K}^{-1})(273.2\ \text{K})}{1.00\ \text{atm}}$$

$V = 22.4\ L\ N_2\ (g)$

$V = 22.4\ L\ H_2\ (g)$

***All gases have the same molar volume (V/n) at the same temperature and pressure. When that temperature and pressure is* STP *the molar volume is* 22.4 L.**

Class Problem: ***What is the volume in liters of 2.8 mol of N_2 (g) at 22.1 ^oC and 753.4 mmHg?***

P = 753.4 mmHg = 753.4 torr

$T = (22.1\ {}^oC + 273.15\ {}^oC)(1K/1^oC) = 295.3\ K$

n = 2.8 mol

$R = 62.36\ torr\text{-}L\text{-}mol^{-1}K^{-1}$

$$PV = nRT$$

$$V = nRT/P = \frac{(2.8\ mol)(62.36\ torr\text{-}L\text{-}mol^{-1}K^{-1})(295.3\ K)}{753.4\ torr}$$

V = 68 L

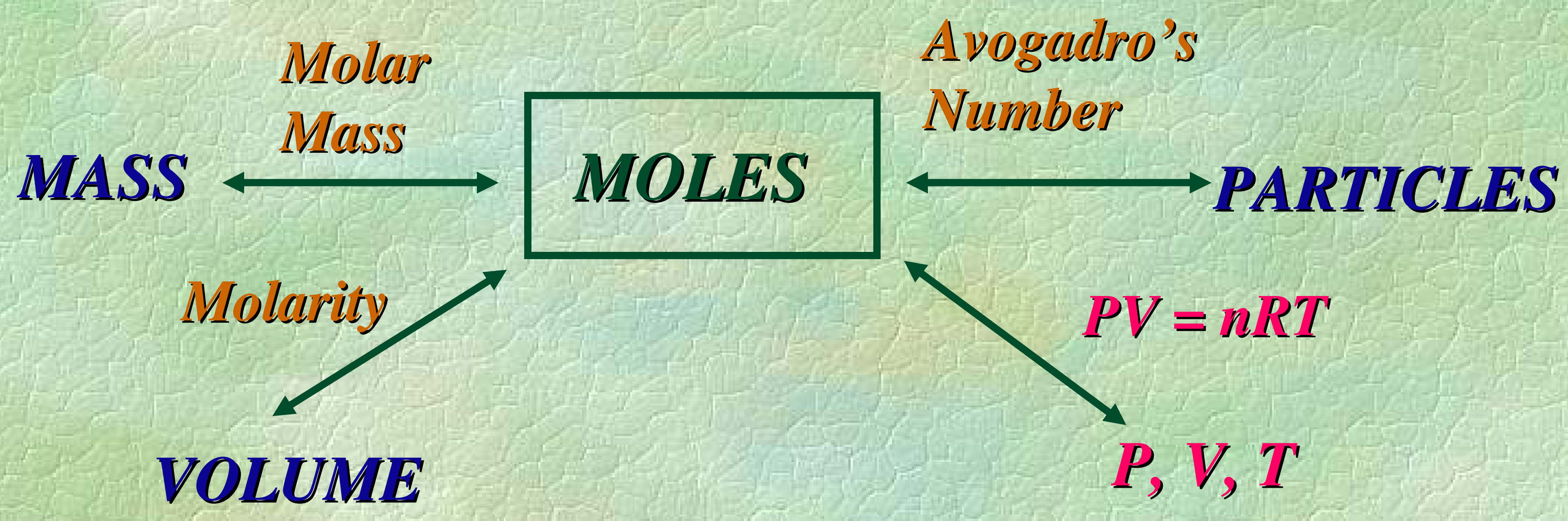
Class Problem: ***A gas occupies 722 mL volume at 32.1°C and 755 torr pressure. How many moles of gas are present?***

$$PV = nRT$$

$$n = PV/RT = \frac{(755\ \text{torr})(0.722\ \text{L})}{(62.36\ \text{torr-L-mol}^{-1}\text{K}^{-1})(305.3\ \text{K})}$$

$$n = 0.0286\ \text{mol}$$

When in Doubt, Calculate Moles!



PV = nRT = (mass/molar mass)RT

$$\frac{PV}{RT} = \frac{\text{mass}}{\text{molar mass}} = \frac{\text{grams}}{\text{grams/mol}}$$

Class Problem: ***A 0.360 g sample of gas occupies 100.0 mL at 300 K and 1.013 atm pressure. What is its molar mass?***

$$\frac{PV}{RT} = \frac{\text{mass}}{\text{molar mass}}$$

$$\text{molar mass} = \frac{(\text{mass})RT}{PV}$$

$$\text{molar mass} = \frac{(0.360\ \text{g})(0.0821\ \text{L-atm-mol}^{-1}\text{K}^{-1})(300\ \text{K})}{(1.013\ \text{atm})(0.1000\ \text{L})}$$

$$\text{molar mass} = 87.5\ \text{g/mol}$$

Gay-Lussac's Law of Combining Volumes: **At constant temperature and pressure, the volumes of gases involved in chemical reactions are in ratios of small whole numbers.**

Avogadro's Hypothesis: **Equal volumes of different gases at the same temperature and pressure contain the same number of *MOLECULES*.**

$$N_2 (g) + 3 H_2 (g) \longrightarrow 2 NH_3 (g)$$

1 Molecule + 3 Molecules 2 Molecules

1 Mole + 3 Moles 2 Moles

1 Volume + 3 Volumes 2 Volumes

***The Mystery of the Diatomic Molecule:* Suppose that hydrogen and chlorine were both "monatomic".**

1 Volume* + *1 Volume* *2 Volumes

¿¿ ¿ H (g) + Cl (g) $\longrightarrow$ 2 HCl (g) ???

This would require "Splitting" the atoms!

But What IF…..

1 Volume* *1 Volume* *2 Volumes

Concept:

A container holds nitrogen gas at 0.10 atm pressure. Suppose enough hydrogen gas was added to increase the pressure to 0.50 atm and then enough oxygen gas was added to increase the total pressure to 1.00 atm. What would be the partial pressure of the three gases?

1. N_2 - 0.10 atm; H_2 - 0.50 atm; O_2 - 1.00 atm

2. N_2 - 0.10 atm; H_2 - 0.40 atm; O_2 - 0.50 atm

3. N_2 - 0.33 atm; H_2 - 0.33 atm; O_2 - 0.33 atm

Dalton's Law of Partial Pressures: **The total pressure of a mixture of gases is equal to the sum of the partial pressures of the individual gases.**

$$P_{total} = P_A + P_B + P_C + \ldots .$$

$$P_{total} = \frac{n_A RT}{V} + \frac{n_B RT}{V} + \frac{n_c RT}{V}$$

$$P_{total} = (n_A + n_B + n_C \ldots .) \frac{RT}{V}$$

Partial Pressure: ***The pressure that a particular gas would exert on the container if it were in the container by itself.***

Class Problem: ***What is the total pressure of a mixture of N_2 and O_2 gases if the partial pressure of N_2 is 0.362 atm and the partial pressure of O_2 = 0.279 atm?***

$P_{total} = P_{Nitrogen} + P_{oxygen}$ = 0.362 atm + 0.279 atm

= **0.641 atm**

Class Problem: ***What is the total pressure in atm of a mixture of 5.83 mol Ar and 2.76 mol H_2 in a 3.75 L container at 752 K?***

$P_{total} = n_{total}$ RT/V =

141 atm

$$\frac{(5.83\ \text{mol} + 2.75\ \text{mol})(0.0821\ \text{L-atm/mol-K})(752\ \text{K})}{3.75\ \text{L}} =$$

Collecting gases over water:

$P_{total} = P_{gas} + P_{water\ vapor}$

Class Problem: ***A sample of H_2 (g) is collected over H_2O at 23.0^oC. The total pressure is 740 torr. What is the partial pressure of H_2 (g)?***

$P_{total} = P_{hydrogen} + P_{water\ vapor}$

$P_{hydrogen} = P_{total} - P_{water\ vapor}$ = 740 torr - 21.3 torr*

= 719 torr

*** Table 5.4***

Class Problem: ***A sample of HgO (s) is decomposed to Hg (l) and O_2 (g). The O_2 (g) is collected over water at 21°C and the total pressure is 765 mmHg. A 250 mL sample of O_2 (g) was collected. What was the mass of the HgO (s) decomposed?***

When in Doubt, Calculate Moles!

	? g		21°C, 250 mL, 765 torr, over H_2O
Problem:			
Equation:	*2 HgO (s)*	⟶	*2 Hg (l) + O_2 (g)*
Formula Masses, u:	*216.59*		

$P_{\text{water vapor}}$ = 18.65 torr @ 21°C

$P_{\text{oxygen}} = P_{\text{total}} - P_{\text{water vapor}}$ = 765 torr - 18.65 torr = 746 torr

T = (21°C + 273.2°C)(1 K/1°C) = 294 K

$PV = nRT$

$$n = PV/RT = \frac{(746\ \text{torr})(0.250\ \text{L})}{(62.36\ \frac{\text{L-torr}}{\text{mol-K}})(294\ \text{K})}$$

$n = 0.010\ 1\underline{7}\ mol\ O_2$

$$(0.010\ 1\underline{7}\ \text{mol}\ O_2)\frac{(2\ \text{mol HgO})}{(\text{mol}\ O_2)}\frac{(216.59\ \text{g HgO})}{(\text{mol HgO})}$$

= 4.41 g HgO

Graham's Law of Effusion: **The rates of effusion of two gases at the same temperature and pressure are inversely proportional to the square roots of their molar masses.**

Effusion: **The process of a gas passing through a small, sometimes molecular-sized, opening.**

Diffusion: **The spreading of one gas throughout another.**

$$r_a \propto (1/mm_a)^{1/2} \qquad r_b \propto (1/mm_b)^{1/2}$$

$$\frac{r_a}{r_b} = \frac{(mm_b)^{1/2}}{(mm_a)^{1/2}}$$

Concept:

Under what conditions of temperature and pressure do **REAL** *gases behave as though they were* **IDEAL** *gases ?*

1. *High Pressure and Low Temperature*

2. *High Pressure and High Temperature*

3. *Low Pressure and High Temperature*

Real gases do not obey the ideal gas laws perfectly because real molecules, atoms, and ions DO HAVE volume and they DO attract one another. However, under conditions of relatively low pressure the molecules are quite far apart and thus, they occupy a small fraction of the total space in the container. Under conditions of relative high temperature the molecules are moving faster that at low temperatures. This causes a reduction in the effects of the attractive forces among them.

"REAL" gases, then behave as "IDEAL" gases under conditions of relatively **LOW PRESSURE** ***and*** **HIGH TEMPERATURE.**

1 atm pressure and 25°C are LOW PRESSURE ***and*** **HIGH TEMPERATURE, respectively. Thus, under these "normal" conditions, real gases behave very much as if they were ideal gases.**

What happens when the pressure is relatively high and the temperature is relatively low?

A "Reality Check": **As the temperature decreases and/or the pressure increases, real gases begin to *DEVIATE* from ideal behavior, the molecules themselves begin to take up a higher percentage of the total volume of the container *and* they their attraction for one another increases.**

1. Compressibility Factor

$PV = nRT$ $\qquad \frac{PV}{nRT} = 1$ (for ideal gas)

$\frac{PV}{nRT} < 1$ means $PV < nRT$ $\qquad \frac{PV}{nRT} > 1$ means $PV > nRT$

For PV < nRT: **Molecular attractions become important, reducing the "effective" pressure.**

For PV > nRT: **The actual volume of the molecules becomes a significant fraction of the volume of the container, causing more collisions with the walls of the container. This will increase the pressure or the volume or both.**

These are competing effects that, at times, exactly offset one another.

2. Van der Waals Equation

$$PV = nRT$$

$$[P + an^2/V^2][V - nb] = nRT$$

***a** is a measure of the intermolecular attractive forces and **b** is a measure of molecular size.*

See Table on page of your textbook