The Gas State

- Gases are everywhere atmosphere, environmental processes, industrial processes, bodily functions
- Gases have unique properties from liquids and solids
- Gases are compressible (very important for storage)
- Gas particles are widely separated and move at very fast speeds
- Most gases have relatively low densities
- Gas have relatively low viscosity (resistance to movement) allowing them move freely through pipes and even small orifices

The Gas State

- Chemical behavior of gases depends on composition
- Physical behavior of all gases is similar
- Gases are miscible mixing together in any proportion
- Behavior of gases described by ideal gas law and kineticmolecular theory, the cornerstone of this chapter
 - Gas volume changes greatly with pressure
 - Gas volume changes greatly with temperature
 - Gas volume is a function of the amount of gas

Introduction to Pressure

- To understand gases, we must first define *force* and *pressure* (primary metric for gases)
- *Force* (F) is a function of the mass of an object under acceleration, such as the force of gravity on masses
 F = mass <u>x acceleration of gravity</u> = <u>m x a</u>
- Pressure (P) is the Force (F) exerted per unit area of surface by molecules in motion

$\mathbf{P} = \mathbf{Force}/\mathbf{unit} \ \mathbf{area} = \mathbf{F} / \mathbf{A}$

Introduction to Pressure



Ways to Measure Pressure
 Barometer – device for measuring pressure of the atmosphere

Manometer – device for measuring the pressure of a gas or liquid in a vessel

Barometric Pressure involves the acceleration due to gravity (g), the density (d) of a liquid in the monometer column and the height (h) of the liquid in the column

P = g d h

Ways to Measure Pressure





The Empirical Gas Laws

- Gas behavior can be described by pressure (P), temperature (T), volume (V), and molar amount (n)
- Holding any two of the variables constant allows relations between the other two

Boyle's Law

The volume of a sample of gas at a given temperature varies inversely with the applied pressure

 $V \propto 1/P \quad (T \& n \text{ are constant})$ PV = Const $P_1V_1 = P_2V_2$ $1/V = a(P) + b \quad (Linear Plot)$

The Empirical Gas Laws Boyle's Law

Two Graphs Illustrating Gas Pressure-Volume Relationship



Boyle's Law

A sample of Chlorine gas has a volume of 1.8 L at 1.0 atm. If the pressure increases to 4.0 atm (at constant temperature), what would be the new volume?

using $P_1V_1 = P_2V_2$ $V_2 = \frac{P_1V_1}{P_2} = \frac{(1.0 \text{ atm}) \times (1.8 \text{ L})}{(4.0 \text{ atm})}$ $V_f = 0.45 \text{ L}$

The Empirical Gas Laws <u>Charles's Law</u>

The volume occupied by any sample of gas at constant pressure is <u>directly</u> proportional to its absolute temperature

> V $\propto T_{abs}$ $T_{abs}(K) = {}^{\circ}C + 273.15$ P & n are constant

Assumes constant moles and pressure

Temperature on absolute scale (°C + 273.15)



V = a(T) + b (Linear Plot)

The Empirical Gas Laws Charles's Law

Linear Relationship of Gas Volume and Temperature at Constant Pressure



Charles's Law

A sample of Methane gas that has a volume of 3.8 L at 5.0°C is heated to 86.0°C at constant pressure. Calculate its new volume.

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

Convert temperature (°C) to Absolute (Kelvin) K $5.0^{\circ}C = 5.0 + 273.15 = 278.15^{\circ}K$ $86.0^{\circ}C = 86.0 + 273.15 = 359.15^{\circ}K$ $V_2 = \left(\frac{T_2}{T_1}\right) V_1 = \left(\frac{359.15 \text{ K}}{278.15 \text{ K}}\right) \times 3.8 \text{ L}$ $V_2 = 4.9 \text{ L}$ The Empirical Gas Laws
 Amontons's Law - Pressure / Temperature relationship
 Charles's Law is expressed as the effect of temperature change on gas volume
 $\frac{V}{T} = constant$

Volume and Pressure are interdependent; therefore the effect of temperature on volume is closely related to its effect on pressure

$$\frac{P}{T} \propto T_{abs} \qquad P \& n \\ \frac{P}{T} = constant$$

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The Empirical Gas Laws

- Combined Gas Law: In the event that all three parameters, P, V, and T, are changing, their combined relationship is defined as follows assuming the mass of the gas (number of moles) is constant Recall:
 - $V \propto 1/P$ PV = constantV/T = constantV oc T $\mathbf{P} \propto \mathbf{T}$ P/T = constant $V \propto \frac{T}{V}$ (PV) / T = constant

The pressure of 4.0 L of Nitrogen in a flexible container is decreased to one-half its original pressure, and its absolute temperature is increased to double the original temperature. The new volume is now

a. 2.0 L b. 4.0 L c. 8.0 L d. 16.0 L e. 32.0 L Ans: d $\frac{P_1V_1}{T_1} (\text{new}) = \frac{P_2V_2}{T_2} (\text{old}) \qquad V_1 = \frac{T_1 \cdot P_2 \cdot V_2}{P_1 \cdot T_2}$ New Pressure (P₁) is equal to 1/2 original pressure $\therefore P_1 = \frac{P_2}{2}$

New Temperature (T₁) is equal to twice orginal temperature \therefore T₁ = 2T₂

$$V_{1} = \frac{T_{1}P_{2}V_{2}}{P_{1}T_{2}} = \frac{2T_{2}P_{2}V_{2}}{\frac{P_{2}}{2}T_{2}} = \frac{2T_{2}P_{2}V_{2}}{\frac{P_{2}T_{2}}{2}} = \frac{4V_{2}V_{2}V_{2}}{\frac{P_{2}T_{2}}{2}} = 4 \times V_{2} = 4 \times 4.0 = 16 L$$

 $5/2.0/2.0^{\circ}$

Avagadro's Law Avogadro's Law

> The volume of a sample of gas is directly proportional to the number of moles of gas, n $\frac{V}{r} \propto n$ $\frac{V}{r} = constant$

Equal volumes of any two gases at the same temperature and pressure contain the same number of molecules (mol)



Avagadro's Law Avogadro's Law

- The volume of <u>one</u> mole of gas is called the: molar gas volume, V_m
- Volumes of gases are often compared at standard temperature and pressure (STP), chosen to be
 - 0 °C (273.15 °K) and 1 atm pressure
 - At STP, the molar volume, V_m, that is, the volume occupied by <u>one mole</u> of any gas, is 22.4 L/mol

$$V_{stp} / n_{stp} = V_m = 22.4 L (at STP)$$

A sample of Fluorine gas has a volume of 5.80 L at 150.0 °C and 10.5 atm of pressure. How many moles of Fluorine gas are present?

First, use the combined Empirical Gas Law to determine the volume at STP. Then, use Avagadro's law to determine the number of moles

$$\frac{V_{stp} P_{stp}}{T_{stp}} (new) = \frac{PV}{T_1} (old)$$

 $V_{\text{STP}} = \frac{\Pr V_{\text{T}} T_{\text{stp}}}{\Pr T_{1}} = \frac{(10.5 \text{ atm}) (5.80 \text{ L}) (273 \text{ K})}{(1.0 \text{ atm}) (423 \text{ K})} = 39.3 \text{ L}$ $\frac{V_{\text{stp}}}{n_{\text{stp}}} = \frac{V_{2}}{n_{2}} = \frac{22.4 \text{ L}}{1 \text{ mol}} = \frac{39.3 \text{ L}}{n} \quad n = 1.75 \text{ mol}$

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The Ideal Gas Law

- This implies that there must exist a proportionality constant governing these relationships
- From the Combined Gas Law, we can obtain the following relationship

$$\mathbf{V}_{\mathbf{m}} = \mathbf{"R"} \times \mathbf{n} \times \left(\frac{\mathbf{T}_{abs}}{\mathbf{P}}\right)$$

where "R" is the proportionality constant referred to as the **Ideal Gas Constant**, which relates Molar Volume (V) to the ratio of Temperature to Pressure T/P

The Ideal Gas Law

The numerical value of "R" can be derived using Avogadro's law, which states that one mole of any gas at STP will occupy 22.4 liters

 $\mathbf{R} = \frac{\mathbf{V} \mathbf{P}}{\mathbf{n} \mathbf{T}}$

 $\mathbf{R} = \frac{(22.4 \text{ L}) (1.00 \text{ atm})}{(1.00 \text{ mol}) (273 \text{ K})}$

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

The Ideal Gas Law
 The ideal gas equation is usually expressed in the following form:

 $\mathbf{PV} = \mathbf{nRT}$

- P Pressure (in atm)
- V Volume (in liters)
- n Number of atoms (in moles)
- R Universal gas constant 0.0821 L[•] atm/mol[•] K
- T Temperature (in °Kelvin = $^{\circ}C$ + 273.15)

Practice Problem A steel tank has a volume of 438 L and is filled with $0.885 \text{ kg of } O_2$. Calculate the pressure of Oxygen in the tank at 21°C Use PV = nRT $\therefore P = \frac{nRT}{V}$ V = 438 L $T = 21^{\circ}C = 21 + 273.15 = 294.15^{\circ}K$ $n = 0.885 \text{ kg O}_2 \text{ (convert to moles)}$ $R = 0.0821 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}}$ n = mol O₂ = 0.885 kg O₂ × $\frac{1000g}{1 \text{ kg}}$ × $\frac{1 \text{ mol O}_2}{32.00 \text{ g O}_2}$ = 27.7 mol O₂ $\mathbf{P} = \frac{\mathbf{nRT}}{\mathbf{V}} = \frac{27.7 \text{ mol O}_2 \times 0.0821 \frac{\mathbf{atm} \cdot \mathbf{L}}{\mathbf{mol} \cdot \mathbf{K}} \times 294.15 \,^{\circ}\mathbf{K}}{438 \, \mathbf{L}} = 1.53 \, \mathrm{atm}$ 5/20/2020

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A 50-L cylinder of Nitrogen, N_2 , has a pressure of 17.1 atm at 23 °C. What is the mass (g) of Nitrogen in the cylinder?

PV = **nRT n** = $\frac{PV}{RT}$ **n** = $\frac{m}{M}$ **R** = 0.0821 $\frac{L \cdot atm}{mol \cdot K}$ V = 50 L P = 17.1 atm T = 23 °C + 273 = 296 °K $M_{m}(N_{2}) = 2 \frac{\text{mol N}}{\text{mol N}_{2}} \times 14.01 \frac{\text{g N}}{\text{mol N}} = 28.02 \frac{\text{g}}{\text{mol N}_{2}}$ $\mathbf{m} = \frac{\mathbf{M}_{\mathbf{m}} \times \mathbf{P} \times \mathbf{V}}{\mathbf{R} \times \mathbf{T}} = \frac{28.02 \frac{\mathbf{g}}{\mathbf{mol}} \times 17.1 \, \mathrm{atm} \times 50 \, \mathrm{L}}{0.0821 \frac{\mathrm{L} \bullet \mathrm{atm}}{\mathrm{mol} \bullet \mathrm{K}} \times 296 \, ^{\circ}\mathrm{K}}$ $m = 985.8 \, g \, N_2$

Ideal Gas Law

Molecular Weight Determination

 If we substitute (mass(m)/Mol Wgt(M_m) = moles (n) in the ideal gas equation, we obtain a direct mathematical expression for the molar mass (molecular weight) of an ideal gas





What is the density of Methane gas (natural gas), CH_4 , at 125 °C and 3.50 atm?

 $\frac{\mathbf{m}}{\mathbf{V}} = \mathbf{d} = \frac{\mathbf{P}\mathbf{M}_{\mathbf{m}}}{\mathbf{R}\mathbf{T}}$ $T = (125^{\circ}C + 273.15) = 398.15^{\circ}K$ P = 3.50 atm $M_{m}(CH_{4}) = 12.01 \frac{gC}{mol C} + 4 \times 1.01 \frac{gH}{mol H} = 16.05 \frac{gCH_{4}}{mol CH_{4}}$ $\mathbf{R} = 0.0821 \frac{\mathbf{L} \bullet \text{atm}}{\text{mol} \bullet \text{K}}$ 3.50 atm × 16.05 g CH₄ $\mathbf{d} = \frac{\mathbf{PM}_{\mathrm{m}}}{\mathbf{RT}} = \frac{1000 \,\mathrm{mL}}{0.0821 \,\mathrm{M} \,\mathrm{M$ $mol CH_4 = 0.00172 \frac{g}{ml}$ m

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Stoichiometry Problem Involving Gas Volumes

Suppose you heat 0.0100 mol of Potassium Chlorate, $KClO_3$, in a test tube. How many liters of Oxygen can you produce at 298 K and 1.02 atm?

Consider the following reaction, which is often used to generate small quantities of Oxygen

$2 \operatorname{KClO}_3(s) \xrightarrow{\Delta} 2 \operatorname{KCl}(s) + 3 \operatorname{O}_2(g)$

Con't on next slide

First we must determine the number of moles of Oxygen produced by the reaction.

$0.0100 \text{ mol KClO}_3 \times \frac{3 \text{ mol O}_2}{2 \text{ mol KClO}_3}$

$= 0.0150 \text{ mol O}_2$

Con't on next slide

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Now we can use the ideal gas equation to calculate the volume of Oxygen under the conditions given.



$V = \frac{(0.0150 \text{ mol O}_2)(0.0821 \frac{L \circ atm}{\text{mol} \circ K})(298 \text{ K})}{1.02 \text{ atm}}$

V = 0.360 L

When a 2.0 Liter bottle of concentrated HCL was spilled, 1.2 kg of CaCO₃ (FW – 100.09) was required to neutralize the spill. What volume of CO₂ was released by the reaction at 735 mm Hg and 20°C? The balanced equation is:

 $CaCO_3(s) + 2 HCl(aq) \rightarrow CaCl_2(aq) + H_2O + CO_2(g)$ Compute moles $CaCO_3$

1.2 kg CaCO₃ $\left(\frac{1000 \text{ g CaCO}_3}{1 \text{ kg CaCO}_3}\right) \left(\frac{1 \text{ mol}}{100.09 \text{ g CaCO}_3}\right) = 11.9892 \text{ mol CaCO}_3$ Molar Ratio CaCO₃ to CO₂ = 1:1 \therefore n = 11.9892 mol CO₂ released Convert pressure to atmospheres 735 mmHg $\left(\frac{1 \text{ atm}}{760 \text{ mmHg}}\right) = 0.9671 \text{ atm}$ $V = \frac{nRT}{P}$ $R = 0.0821 \frac{L \cdot atm}{mol \cdot K}$ $T = 20^{\circ} C + 273.15 = 293.15^{\circ} K$ $\frac{(11.9892 \text{ mol CO}_2)(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}})(293.15 \text{ K})}{0.9671 \text{ atm}} = 298.\text{L}$

Partial Pressures of Gas Mixtures
 Dalton's Law of Partial Pressures: the sum of all the pressures of all the different gases (a, b, c, etc.) in a mixture equals the total pressure of the mixture.

 $\mathbf{P}_{\text{tot}} = \mathbf{P}_{\text{a}} + \mathbf{P}_{\text{b}} + \mathbf{P}_{\text{c}} + \dots$

• The individual pressures follow the ideal gas law $P_a V = n_a R T$ **Partial Pressures of Gas Mixtures**

- The composition of a gas mixture is often described in terms of its mole fraction.
- The mole fraction, X_a, of a component gas is the fraction of moles of that component in the total moles of gas mixture.



Partial Pressures of Gas Mixtures The partial pressure of a component gas, "A", is then defined as



Applying this concept to the *ideal gas equation*, we find that each gas can be treated *independently*



Collecting Gases "Over Water"

- A useful application of partial pressures arises when you collect gases over water
 - As gas bubbles through the water, the gas becomes saturated with water vapor
 - The partial pressure of the water in this "mixture" depends only on the temperature

Collection of Gas Over Water $Zn(s) + 2 HCI \rightarrow ZnCl_2(aq) + H_2(g)$


Practice Problem Suppose a 156 mL sample of H₂ gas was collected over Water at 19°C and 769 mm Hg. What is the mass of H₂ collected? First, find the partial pressure of the dry H₂

 $|\mathbf{P}_{\mathbf{H}_2}| = \mathbf{P}_{\text{tot}} - \mathbf{P}_{\mathbf{H}_2}|$

The vapor pressure of water at 19°C is 16.5 mm Hg

 $P_{H_2} = 769 \text{ mm Hg} - 16.5 \text{ mm Hg}$ $P_{H_2} = 752 \text{ mm Hg}$ Practice Problem (Con't)
 Now use the ideal gas equation, along with the partial pressure of the Hydrogen, to determine its mass

 $P_{H_{1}} = 752 \text{ mm Hg} \times \frac{1 \text{ atm}}{760 \text{ mm Hg}} = 0.989 \text{ atm}$ $V = 156 \,\mathrm{mL} = 0.156 \,\mathrm{L}$ Hydrogen $T = (19 + 273) = 292^{\circ} K$ n = PV / RT = [(0.989 atm)(0.156)] / [(0.0821)(292K)] $= 0.00644 \text{ mol H}_{2}$

 $0.00644 \text{ mol H}_{2} \times 2.016 \text{ g H}_{2} / \text{ mol H}_{2} = 0.013 \text{ g Hydrogen}$

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Conceptual Problem 5.25 Consider the following gas container equipped with a movable piston.



- a. By what factor (increase by 1, decrease by 1.5, etc.) would you change the pressure if you wanted the volume to change from volume C to volume D?
- b. If the piston were moved from volume C to volume A, by what factor would the pressure change?
- c. By what factor would you change the temperature in order to change from volume C to volume B?
- d. If you increased the number of moles of gas in the container by a factor of 2, by what factors would the pressure and the volume change?

PV = const V/T = const V/n = const

PV = nRT

- a. Pressure would <u>increase</u> by a factor of "2"
- b. Pressure would <u>decrease</u> by factor of "2"
- c. Increase temperature by a factor of "1.5"
- d. The volume would <u>increase</u> by a factor of "2"

The pressure would <u>remain</u> <u>the same</u>

Carbon Monoxide, CO, and Oxygen, O₂, react according to:

 $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$ Assuming that the reaction takes place and <u>goes</u> to completion, determine what substances remain, and what their partial pressures are after the valve is opened in the apparatus shown below. Assume that the temperature is fixed at 300 K.



Practice Problem (Con't) $2CO(g) + O_2 \rightarrow 2CO_2(g)$ Stoichiometric Molar Ratio: 2 : $1 \rightarrow 2$ Compute moles CO in first flask PV = nRT $n = \frac{PV}{RT} = \frac{0.500 \text{ atm} \times 2.00 \text{ L}}{300 \text{ K} \times 0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}} = 0.0406 \text{ mol}$ Compute moles O₂ in second flask $PV = nRT \qquad n = \frac{PV}{RT} = \frac{1.00 \text{ atm} \times 1.00 \text{ L}}{300 \text{ K} \times 0.0821} \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} = 0.0406 \text{ mol}$ $\frac{\text{mol CO}}{\text{mol O}_2} = \frac{0.0406}{0.0406} = 1.0$ Actual Molar Ratio Actual ratio (1.0) < Stoichiometric ratio (2.0) \therefore CO is limiting Con't on next Slide Theoretical Yield of CO₂ is 0.0406 mol

Practice Problem (Con't)

Amount of compounds remaining after reaction:

- CO(g) 0.0 mol (Limiting reagent completely consumed)
- $O_2(g)$ 0.0203 mol (only half the O_2 was required to react with CO)
- CO₂(g) 0.0406 mol (based on 0.0405 mol of limiting reagent (CO))

Partial Pressure of O_2 in combined volume (3.0 L)

$$P_{O_2} = \frac{nRT}{V} = \frac{0.0203 \text{ mol} \times 0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 300 \text{ K}}{3.0 \text{ L}} = 0.167 \text{ atm}$$

Partial Pressure of CO₂ in combined volume (3.0 L) $P_{CO_2} = \frac{nRT}{V} = \frac{0.0406 \text{ mol} \times 0.0821 \frac{L \cdot atm}{mol \cdot K} \times 300 \text{ K}}{3.0 \text{ L}} = 0.333 \text{ atm}$

- A 100.0 mL sample of air exhaled from the lungs is analyzed and found to contain 0.0830 g of N₂, 0.0194 g O₂, 0.00640 g CO₂ and 0.00441 g water vapor at 35 °C.
- What is the partial pressure of each component and total pressure of the sample? What is the mole fraction of each component?

Calculate the moles of each gas

 $\frac{1 \text{ mol } N_2}{28.02 \text{ g } N_2}$ $mol N_2 = 0.0830 g N_2$ $= 0.00296 \text{ mol } N_2$ × 1 mol O2 $mol O_2 = 0.0194 g O_2$ $= 0.000606 \text{ mol O}_{2}$ × 32.00 g O₂ 1 mol CO₂ $mol CO_2 = 0.00640 g CO_2 \times$ $= 0.000145 \,\mathrm{mol}\,\mathrm{CO}_{2}$ 44.01 g CO 1 mol H₂O $mol H_2O = 0.00441 g H_2O \times$ $= 0.000244 \text{ mol H}_{2}O$ 18.02 g H₂O Con't on next slide

- A 100.0 mL sample of air exhaled from the lungs is analyzed and found to contain 0.0830 g of N₂, 0.0194 g O₂, 0.00640 g CO₂ and 0.00441 g water vapor at 35 °C.
- What is the partial pressure of each component and total pressure of the sample? What is the mole fraction of each component?

Calculate "Total" Moles

 $n_{tot} = n_{N_{c}} + n_{O_{c}} + n_{CO_{c}} + n_{H,O}$ = 0.00296 mol N₂ + 0.000606 mol O₂ + 0.000145 mol CO₂ + 0.000244 mol H₂O

 $= 0.00396 \, mol$

Calculate "Total" pressure

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$$P_{tot} = \frac{n_{tot}RT}{V} = \frac{0.00396 \text{ mol} \times 0.0821 \frac{L \cdot atm}{mol \cdot K} \times 308 \text{ }^{\circ}\text{K}}{100 \text{ mL} \times \frac{1L}{1000 \text{ mL}}} = 1.00 \text{ atm}$$

$$Con't \text{ on next slide}$$

$$Q20$$

- A 100.0 mL sample of air exhaled from the lungs is analyzed and found to contain 0.0830 g of N₂, 0.0194 g O₂, 0.00640 g CO₂ and 0.00441 g water vapor at 35 °C.
- What is the partial pressure of each component and total pressure of the sample? What is the mole fraction of each component?

Calculate mole fractions

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$$X_{N_{2}} = \frac{n_{N_{2}}}{n_{tot}} = \frac{0.00296}{0.00396} = 0.747 \qquad X_{O_{2}} = \frac{n_{O_{2}}}{n_{tot}} = \frac{0.000606}{0.00396} = 0.153$$
$$X_{CO_{2}} = \frac{n_{CO_{2}}}{n_{tot}} = \frac{0.000145}{0.00396} = 0.037 \qquad X_{H_{2}O} = \frac{n_{H_{2}O}}{n_{tot}} = \frac{0.000244}{0.00396} = 0.063$$

Calculate the Partial Pressure of each gas

 $P_{N_{2}} = X_{N_{2}} * P_{tot} = 0.747 * 1.00 = 0.747 \text{ atm}$ $P_{0_{2}} = X_{0_{2}} * P_{tot} = 0.153 * 1.00 = 0.153 \text{ atm}$ $P_{0_{2}} = X_{0_{2}} * P_{0_{1}} = 0.037 * 1.00 = 0.037 \text{ atm}$ $P_{0_{2}} = X_{0_{2}} * P_{0_{1}} = 0.063 * 1.00 = 0.063 \text{ atm}$

You prepare nitrogen gas by heating Ammonium Nitrite:

 $\frac{\text{NH}_4(\text{NO}_2)(\text{s})}{\text{If you collected the Nitrogen over water at 22 °C and 727}}$ $\frac{\text{M}_4(\text{NO}_2)(\text{s})}{\text{M}_4(\text{NO}_2)(\text{s})} \xrightarrow{\text{M}_2(\text{g})}{\text{M}_2(\text{g})} + \frac{2\text{H}_2O(\text{I})}{2\text{H}_2O(\text{I})}$

Compute Moles of NH₄NO₂

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 $mol \, NH_4 NO_2 = n = 5.68g \times \frac{1 \, mol \, NH_4 NO_2}{64.06 \, g \, NH_4 NO_2} = 0.0887 \, mol \, NH_4 NO_2$ $Molar \, Ratio \quad \frac{NH_4 NO_2}{N_2} = 1:1 \quad \therefore \ 0.0887 \, mol \, N_2 \, produced$ $C \, ompute \, Partial \, Pressure \, of \, Nitrogen \, Gas$ $P_{N_2} = P_{tot} - P_{H_2O} = 727 \, mm \, Hg - 19.8 \, mm \, Hg = 707.2 \, mm \, Hg$ $V = \frac{nRT}{P} = \frac{0.0887 \, mol \, N_2 \times 0.0821 \times \frac{L * atm}{mol * K} \times 295^0 \, K}{707.2 \, mm \, Hg \times \frac{1 \, atm}{760 \, mm \, Hg}} = 2.31 \, L$

Kinetic-Molecular Theory of Gases

- A simple model based on the actions of individual atoms
 - Gases consist of particles in constant motion
 - Pressure derived from bombardment with container
 - > Kinetic energy described as $E_k = \frac{1}{2} mv^2$
- Postulates of Kinetic Theory
 - Volume of particles is negligible
 - Particles are in constant motion
 - No inherent attractive or repulsive forces
 - The <u>average</u> kinetic energy of a collection of particles is proportional to the temperature (K)

 $\overline{E_k} \propto T$ or $\overline{E_k} = c \times T$ (c is a constant that is the same for any gas)

Kinetic-theory Model of Gas Pressure

- Another approach to the Ideal-gas Equation
 - A gas consists of molecules in constant motion
 - Gas Pressure (P) is proportional to the frequency of molecular collisions and the average force exerted by a molecule in collision
 - \succ Thus, P \propto rate of collision x avg force of molecule collision
 - "rate of collision" is proportional to the no. particles per unit volume (N/V) and their speed (u)
 - "avg force" depends on momentum (m * u)

 \therefore P \propto (u x N/V) x mu

$PV \propto Nmu^2$

Since the average kinetic energy (1/2 mu²) is proportional to Temperature (T); then mu² \propto T, i.e., energy related to Temp The number of particles (N) can be represented as moles (n), PV \propto nT PV = nRT

Recall that the <u>average</u> kinetic energy of a collection of particles is proportional to the temperature (K)

 $\overline{E_k} \propto T$ or $\overline{E_k} = c \times T$ (c is a constant that is the same for any gas)

The constant "c" has been shown to be:

$$c = \frac{3}{2} \left(\frac{R}{N_A} \right)$$
$$\overline{E_k} = \frac{3}{2} \left(\frac{R}{N_A} \right) T$$

Where "R" is the Universal Gas Constant "N_A" is Avogadros Number

Temperature is related to the <u>average</u> (not "total") energy of molecular motion

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From the general expression for kinetic energy of an object $E_k = \frac{1}{2}mass \times velocity^2 = \frac{1}{2}mv^2$ The average kinetic energy of each molecule in a large population is: $\overline{E_k} = \frac{1}{2}m\overline{u^2}$ Therefore: $\frac{1}{2}m\overline{u^2} = \frac{3}{2}\left(\frac{R}{N_*}\right)T$

 $N_A m \overline{u^2} = 3RT$

 $N_A m = Avogadros Number \times Molecular Mass = Molar Mass (M)$

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

The root-mean-square (rms) molecular speed, u, is a type of average molecular speed, equal to the speed of a molecule having the average molecular kinetic energy.

The square root of the previous equation gives:

 $\frac{3RT}{M}$

Unit relationships

- R = 8.314 kg•m²/s²/mol•K
- T = Temperature (K)
- $M_m = kg/mol$ (Molar Mass)
- 1 Joule = $kg \cdot m^2/s^2$
 - = 8.314 J/mol•K

 μ (rms) = m/s

R

What is the ratio of the average speed of CH_4 (MW = 16 g/mol) molecules to that of SO_2 (MW = 64 g/mol) molecules at 298 K? $R = 8.314 \text{ J/(mol} \cdot \text{K}) = 8.314 \text{ kg} \cdot \text{m}^2/\text{s}^2/\text{mol} \cdot \text{K})$ a. 1:2 b. 1:1 c. 2:1 d. 3:2 e. 1:3 Ans: $C = \sqrt{\frac{3RT}{M_{m}}}$ $R = 8.314 \frac{\text{km} \cdot \text{m}^2}{\text{mol} \cdot \text{K}}$ Molar Mass (Mm) - kg / mol $\mu (CH_4) = \sqrt{\frac{3 \left(8.314 \frac{\text{km} \cdot \text{m}^2}{\text{mol} \cdot \text{K}}\right) (298 \,^{\circ}\text{K})}{\frac{16 \,\text{g} \, CH_4 \frac{1 \,\text{kg}}{1000 \,\text{g}}}}} = 681.6 \,\text{m/s}$ $\frac{681.6}{340.8} = \frac{2}{1}$ 1 mol CH₄ $\mu (SO_2) = \sqrt{\frac{3 \left(8.314 \frac{\text{km} \cdot \text{m}^2}{\text{mol} \cdot \text{K}} \right) (298 \,^{\circ}\text{K})}{\frac{64 \,\text{g} \,\text{SO}_2 \frac{1 \,\text{kg}}{1000 \,\text{g}}}}} = 340.8 \,\text{m/s}$ 1 mol SO, 5/20/2020

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Kinetic-theory Model of Gas Diffusion

Diffusion = process whereby a gas spreads out through another gas to occupy the space uniformly

Chemicals move from high concentration to low concentration



Diffusion is the transfer of a gas through space or another gas over time

Effusion is the transfer of a gas through a membrane or orifice

The equation for the rms velocity of gases shows the following relationship between rate of effusion and molecular mass.



- Effusion is the process in which individual molecules flow through a hole without collisions between molecules.
- This occurs if the diameter of the hole is considerably smaller than the mean free path of the molecules.

According to Graham's law, the rate at which gases effuse (i.e., how many molecules pass through the hole per second) is dependent on their molecular weight; gases with a lower molecular weight effuse more quickly than gases with a higher molecular weight.

For two gases at the same temperature (and having the same specific heat), and thus having the same kinetic energy, the root mean square molecular speed, of each gas can be found using the equation

$$\frac{3}{2}\mathbf{k_bT} = \frac{1}{2} \times \mathbf{Mm} \times \mathbf{v_{rms}^2}$$

where $k_h = Boltzman Constant k = 1.38066 \times 10^{-23} J / K$

T = Temperature (K)

Mm = **Molecular** mass of particle

v = Root Mean Square Velocity (rms)

Which of the following gases will have the *slowest rate of effusion?*

(assume they are all at the same temperature):

b. F_2 c. H_2 d. Ne e. SO_3 a. CH_4 Ans: e Rate of effusion \propto - $\frac{1}{\sqrt{\text{Mm CH}_4}} = \frac{1}{\sqrt{16}} = 0.25$ $M_m CH_4 = 12 + 4 \times 1.0 = 16 \text{ g/mol}$ $\frac{1}{\sqrt{Mm F}} = \frac{1}{\sqrt{38}} = 0.162$ $M_m F_2 = 2 \times 19.00 = 38 \text{ g/mol}$ $\frac{1}{\sqrt{Mm H_2}} = \frac{1}{\sqrt{2}} = 0.707$ $M_m H_2 = 2 \times 1.0 = 2 g/mol$ $\frac{1}{\sqrt{Mm Ne}} = \frac{1}{\sqrt{20}} = 0.223$ $M_{m} Ne = 1 \times 20.18 = 20 g/mol$ $M_m SO_3 = 32 + 3 \times 16 = 80 \text{ g/mol}$ $=\frac{1}{\sqrt{80}} = 0.112$ 5/20/2020

Graham's law

The rate of effusion or diffusion is inversely proportional to the square root of its molecular mass

 $\frac{\text{Rate of effusion of gas "A"}}{\text{Rate of effusion of gas "B"}} = \sqrt{\frac{M_m \text{ of gas B}}{M_m \text{ of gas A}}}$

Greenhouse Effect of Certain Gases in the Atmosphere



- Gases deviate from ideal behavior because the ideal gas law assumes that the molecules of the gas have no volume of their own, and that there are no interactions between the gas molecules
- Under low pressure conditions, the volume of space actually occupied by the molecules is minimized because there are fewer gas molecules present
- At higher temperatures, i.e., above 273 °K (0°C), interactions between the gas molecules are minimized because the energy of the molecules is higher than the intermolecular forces of interactions between the molecules

Real gases, as opposed to "Ideal Gases" do not act as "infinitesimal" points of mass

Real gases have volumes determined by the sizes of their molecules, and the length and direction of their bonds

Atoms in gases contain charged particles and many bonds are polar giving rise to attractive and repulsive forces.

These real properties cause gases to: Deviate from "Ideal Behavior"

- At ordinary conditions of relatively high temperature and low pressure, most gases exhibit "nearly" ideal behavior
- Even at Standard Temperature & Pressure (STP), most gases deviate only slightly from ideal behavior

Gas	Molar Volume (L/mol)	Condensation Poir (°C)
Не	22.435	-268.9
H ₂	22.432	-252.8
Ne	22.422	-246.1
Ideal gas	22.414	
Ar	22.397	-185.9
N ₂	22.396	-195.8
$\overline{O_2}$	22.390	-183.0
CO	22.388	-191.5
Cl ₂	22.184	-34.0
NH ₃	22.079	-33.4

Molar Volume of Some Common Gases At STP (0°C & 1 atm)

At pressures greater than 10 atm, gases deviate significantly from ideal behavior

- For <u>1 mole</u> at moderately high pressure, values of PV/RT) lower than ideal (less than "1") are due predominately to <u>"Intermolecular Attractions"</u>
- At very high pressure, values of PV/RT greater than ideal (more than "1") are due primarily to



"<u>Molecular Volume</u>"

Intermolecular Attractions

- Attractive Forces between molecules are much weaker than the covalent bonding forces that hold a molecule together
- Most Intermolecular Attractions are caused by slight imbalances in electron distribution and are important only over relatively short distances
- At normal pressures the spaces between molecules of any real gas are so large that attractions are negligible
- As pressure rises, the intervening distances are much shorter and the attractions have a greater impact
- Increased attractions decrease force of collisions on container wall, lowering pressure, which results in a smaller numerator in the PV/RT term (PV/RT < 1)</p>

Molecular Volume

- At normal pressures, the space between molecules is very large compared to the volumes of molecules themselves (molecular volume)
- Free volume is essentially equal to the volume of the container
- At higher pressures, the free volume decreases as the molecular volume makes up a greater proportion of the container volume
- Since the volume of the container (V) does not change, the ratio of the PV/RT term is artificially high (PV/RT > 1)
- The molecular volume effect outweighs the intermolecular attraction effect as the pressure increases

Effect of Intermolecular attractions on measured gas pressure

Intermolecular attractions <u>decrease</u> the force of collision with the wall, reducing actual pressure, thus the numerator in the PV/RT term is <u>reduced</u> (PV/RT < 1 for 1 mole)

At higher pressures, the free volume becomes significantly less than the container volume, thus the ratio of the PV/RT term is artificially high 5/20/2020 PV/RT > 1 for 1 mole)



Effect of Molecular Volume on measured gas pressure



Van der Waals Equation
 The "Ideal Gas Law" equation must be redesigned to do two things

Adjust the measured pressure up by adding a factor that accounts for intermolecular attraction

Adjust the measure volume down by subtracting a factor from the entire container volume (V) that accounts for the molecular volume

Van der Waals Equation

Van der Waals Equation

Van der Waals Constants (a & b)

(V-nb) = nRTadjusts adjusts V down P up Ρ - measured pressure V measured Volume Ν - Amount (moles) - Universal Gas Constant R – Temperature (⁰K) Т a & b – Van der Waals Constants

a & b = 0 for ideal gas

adjusts P up adjusts V down atm*L² mo He 0.034 0.0237 Ne 0.211 0.0171 1.35 0.0322 Ar 2.32 0.0398 Kr 4.19 0.0511 Xe H_2 0.244 0.0266 N_2 1.39 0.0391 $O_2^ Cl_2$ 1.36 0.0318 6.49 0.0562 CH_4 0.0428 2.25 CO 1.45 0.0395 CO_2 3.59 0.0427 NH_3 4.17 0.0371 H_2O 5.46 0.0305

A person exhales about 5.8 x 10^2 L of carbon dioxide (MW = 43.999) per day (at STP). The CO₂ exhaled by an astronaut is absorbed from the air of a space capsule by reaction with Lithium Hydroxide, LiOH.

 $2 \text{ LiOH}(s) + \text{CO}_2(g) \rightarrow \text{Li}_2\text{CO}_3(s) + \text{H}_2O(l)$

How many grams of LiOH (FW = 23.943) are required per astronaut per day?

 $5.8 \times 10^{2} \text{ L CO}_{2} / \text{day} \left(\frac{1 \text{ mol}}{22.4 \text{ L}}\right) \left(\frac{2 \text{ mol Li(OH)}}{1 \text{ mol CO}_{2}}\right) \left(\frac{23.943 \text{ g Li(OH)}}{1 \text{ mol Li(OH)}}\right)$

12. g Li(OH) / day

A sample contained a mixture of $CaCO_3$ and $BaCO_3$. The amount of $CaCO_3$ was determined by reacting 7.80 g of the sample with an excess of HCl to release CO_2 from each compound:

$CaCO_3 + 2 HCI \rightarrow CaCl_2 + CO_2(g)$

$BaCO_3 + 2 HCI \rightarrow BaCl_2 + CO_2(g)$

If the sample reacted completely and produced 1,701.42 mL of CO₂ at 29.06 °C and 752.3 mm Hg, what was the mass percentage of CaCO₃ in the mixture?

Practice Problem (Con't)

Total Mass Sample = $m_{BaCO_1} + m_{CaCO_2} = 7.80 \text{ g}$

Volume CO₂ Produced = 1701.42 mL at 29.06 °C and 752.3 mm Hg



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A gaseous mixture of (Propane) C_3H_8 and SO_2 has a density of 2.317 g/L at -1.0 °C and 746.6 mm Hg.

What is the mass percent of C_3H_8 ?

PV = nRT $PV = \frac{m}{M_m}RT$ $\frac{m}{V} = d = \frac{M_m * P}{RT}$ $d_{mix} = \frac{m_{C_{3}H_{8}}}{V_{mix}} + \frac{m_{SO_{2}}}{V_{mix}} = \frac{M_{m_{C_{3}H_{8}}}P_{C_{3}H_{8}}}{RT} + \frac{M_{m_{SO_{2}}}P_{SO_{2}}}{RT}$ $\mathbf{P}_{\text{tot}} = \mathbf{P}_{\mathbf{C}_{3}\mathbf{H}_{8}} + \mathbf{P}_{\mathbf{SO}_{3}}$ $\frac{d_{mix}}{P_{tot}} = \frac{1}{RT} \times \frac{\left(M_{m_{C_{3}H_{8}}}P_{C_{3}H_{8}}\right) + \left(M_{m_{SO_{2}}}P_{SO_{2}}\right)}{P_{tot}}$ mole fraction $C_3H_8 = X_{C_3H_8} = \frac{P_{C_3H_8}}{P_{tot}}$ mole fraction $SO_2 = X_{SO_2} = \frac{P_{SO_2}}{P_{tot}}$ Con't on next slide $X_{C_{3}H_{8}} + X_{SO_{2}} = 1$ $\therefore X_{C_{3}H_{8}} = 1 - X_{SO_{2}}$ 5/20/2020
Practice Problem (Con't)

A gaseous mixture of C_3H_8 and SO_2 has a density of 2.317 g/L at -1.0 °C and 746.6 mm Hg.

What is the mass percent of C_3H_8 ?

$$\frac{\mathbf{d}_{\text{mix}}}{\mathbf{P}_{\text{tot}}} = \frac{1}{\mathbf{RT}} \begin{bmatrix} \frac{\left(\mathbf{M}_{\text{m}_{C_{3}\text{H}_{8}}} \mathbf{P}_{c_{3}\text{H}_{8}}\right) + \left(\mathbf{M}_{\text{m}_{SO_{2}}} \mathbf{P}_{sO_{2}}\right)}{\mathbf{P}_{\text{tot}}} \end{bmatrix} \qquad \frac{\mathbf{d}_{\text{mix}}}{\mathbf{P}_{\text{tot}}} = \frac{1}{\mathbf{RT}} \begin{bmatrix} \mathbf{M}_{\text{m}_{C_{3}\text{H}_{8}}} \left(1 - \mathbf{X}_{sO_{2}}\right) + \mathbf{M}_{\text{m}_{SO_{2}}} \mathbf{X}_{sO_{2}} \end{bmatrix} \qquad \mathbf{N}$$

mol • K

$$\mathbf{X}_{\mathrm{so}_{2}} = \frac{\frac{\mathbf{d}_{\mathrm{mix}} \mathbf{K} \mathbf{I}}{\mathbf{P}_{\mathrm{tot}}} - \mathbf{M}_{\mathrm{m}_{\mathrm{C}_{3}\mathrm{H}_{8}}}}{\mathbf{M}_{\mathrm{m}_{\mathrm{SO}_{2}}} - \mathbf{M}_{\mathrm{m}_{\mathrm{C}_{3}\mathrm{H}_{8}}}}$$

2.317 g / L × 0.0821

746.6 mm Hg

$$\frac{\mathbf{d}_{mix}}{\mathbf{P}_{tot}} = \frac{1}{\mathbf{RT}} \left[\left(\mathbf{M}_{m_{C_3H_8}} \mathbf{X}_{C_3H_8} \right) + \left(\mathbf{M}_{m_{SO_2}} \mathbf{X}_{SO_2} \right) \right]$$

 $Mm_{C_3H_8}$ - Molar Mass C_3H_8

Mm_{SO2} - Molar Mass SO₂

 $X_{C_3H_8}$ - Mole Fraction C_3H_8

$$X_{C_{3}H_{8}} + X_{SO_{2}} = 1.0$$

$$\mathbf{X}_{\mathbf{C}_{3}\mathbf{H}_{8}} = \mathbf{1} - \mathbf{X}_{\mathbf{SO}_{2}}$$

1 atm

760 mm Hg

× 272.15 °K

= 1 - 0.43 = 0.5697

$$X_{so_2} = 0.4303$$

X_{so}

Con't on next slide

Practice Problem (con't) A gaseous mixture of C_3H_8 and SO_2 has a density of 2.317 g/L at -1.0 °C and 746.6 mm Hg. What is the mass percent of C_3H_8 ? Mole Fractions: $X_{C_3H_8} = 1 - 0.4303 = 0.5697$ $X_{so_{2}} = 0.4303$ Assume total moles in sample = 1 $\therefore 0.5697 \, \text{mol} \, C_{H} = 0.4303 \, \text{mol} \, SO_{H}$ Mass $C_{3}H_{8} = 0.5697 \text{ mol } C_{3}H_{8} \times \frac{44.11 \text{ g } C_{3}H_{8}}{\text{ mol } C \text{ H}} = 25.1295 \text{ g } C_{3}H_{8}$ Mass SO₂ = 0.4303 mol SO₂ × $\frac{64.07 \text{ g SO}_2}{\text{mol SO}}$ = 27.5693 g SO₂ Total Mass = 25.1295 + 27.55 = 52.5693 g Mass % $C_{_3}H_{_8} = \frac{25.1295}{52.5693} = 47.80 \times 100 = 48\%$

5/20/2020

Equation Summary		
Force:	F = mass x accelera	tion of gravity = m x a
Pressure:	P = force/unit area	$= \mathbf{F} / \mathbf{A}$
Manometer liquic	is: $\frac{\mathbf{h}_{\text{Decane}}}{\mathbf{h}_{\text{Hg}}} = \frac{\mathbf{d}_{\text{Hg}}}{\mathbf{d}_{\text{Decane}}}$	
Boyle's Law:	$\mathbf{PV} = \mathbf{constant}$	$\mathbf{P}_1\mathbf{V}_1 = \mathbf{P}_2\mathbf{V}_2$
Charles's Law:	$\frac{\mathbf{V}}{\mathbf{T}} = \mathbf{constant}$	$\frac{\mathbf{V}_1}{\mathbf{T}_1} = \frac{\mathbf{V}_2}{\mathbf{T}_2}$
Combined Law:	$\frac{\frac{P_{1}V_{1}}{T_{1}}}{\frac{P_{1}V_{2}}{T_{2}}} = \frac{\frac{P_{2}V_{2}}{T_{2}}}{\frac{P_{2}V_{2}}{T_{2}}}$	
Avagadro's Law:	V ∝ n	$\frac{\mathbf{V}}{\mathbf{n}} = \mathbf{constant}$
Ideal Gas Law:	$\mathbf{PV} = \mathbf{nRT} \qquad \mathbf{n} = \frac{\mathbf{PV}}{\mathbf{RT}}$	$n = \frac{m}{M_{m}}$ $R = 0.0821 \frac{L \cdot atm}{mol \cdot K}$
5/20/2020	$PV = \left(\frac{m}{M_m}\right) RT$	$\frac{\mathbf{m}}{\mathbf{V}} = \mathbf{d} = \frac{\mathbf{PM}_{\mathbf{m}}}{\mathbf{RT}}$

