

Chemistry 121: Topic 5 - The Gaseous State

Topic 5 The Gaseous State:

- 5.1 Empirical approach to the gas laws.
- 5.2 Application of the gas laws to reaction stoichiometry. Dumas method etc.
- 5.3 The Kinetic Molecular Theory of gases
- 5.4 Ideal versus real gases



Chemistry 121: Topic 5 - The Gaseous State

Properties of Gases:

- Gases assume the volume and shape of their containers.
- Gases are the most compressible of the states of matter.
- Gases will mix evenly and completely when confined to the same container.
- Gases have much lower densities than liquids and solids.

Table 5.1 Some Substances Found as Gases at 1 atm and 25°C

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

* The boiling point of HCN is 26°C, but it is close enough to qualify as a gas at ordinary atmospheric conditions.

Chemistry 121: Topic 5 - The Gaseous State

Key Terms and Units:

Pressure: defined as force per unit area

SI units for Force is the newton (N) or $1 \text{ N} = 1 \text{ kg m/s}^2$

The SI unit for Pressure is the **Pascal (Pa)**; $1 \text{ Pa} = 1 \text{ N/m}^2$

Atmospheric Pressure is the pressure exerted by the Earth's Atmosphere

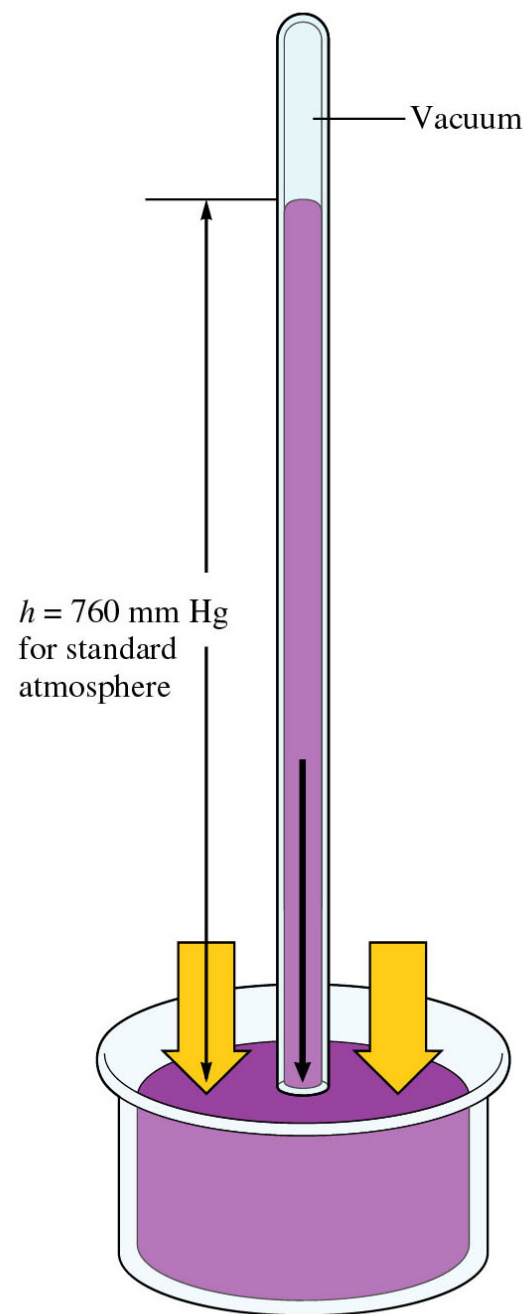
A **Barometer** is an instrument for measuring pressure

Standard Atmospheric Pressure (1 atm) is equal to the pressure that supports a column of mercury exactly 760 mm (or 76 cm) high at 0°C at sea level

$$1 \text{ torr} = 1 \text{ mm Hg} = 1 \text{ atm}$$

$$1 \text{ atm} = 101,325 \text{ Pa} = 1.01325 \times 10^5 \text{ Pa}$$

A **manometer** is a device used to measure pressures of gases other than the atmosphere.



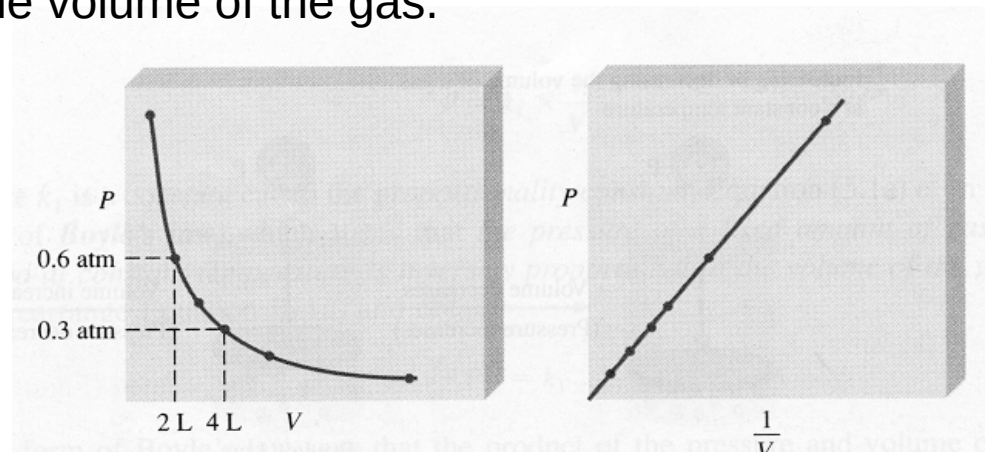
Chemistry 121: Topic 5 - The Gaseous State

Empirical Gas Laws:

Boyle's Law: Pressure of a fixed amount of gas maintained at constant temperature is inversely proportional to the volume of the gas.

$$P \propto \frac{1}{V} \quad \text{or} \quad PV = k$$

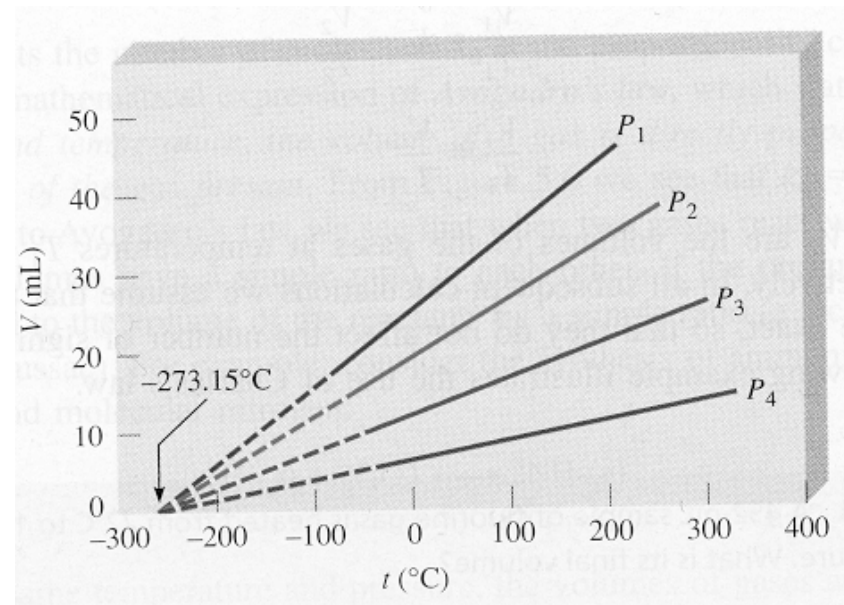
$$P_1V_1 = P_2V_2$$



Charles and Gay-Lussac's Law: the volume of a fixed amount of gas maintained at a constant pressure is directly proportional to the absolute temperature of the gas.

$$P \propto T \quad P \propto \frac{1}{V} \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Based on Charles Law, Lord Kelvin identified -273.15°C as **absolute zero**. The basis for the **absolute temperature** or **Kelvin** temperature scale.

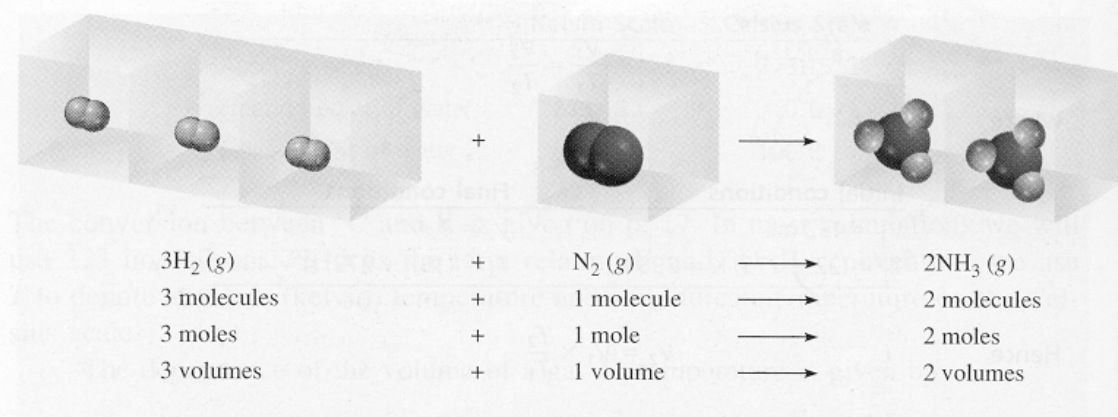
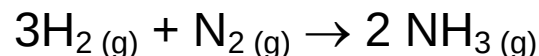


Chemistry 121: Topic 5 - The Gaseous State

Avogadro's Law: at constant pressure and temperature, the volume of a gas is directly proportional to the number of moles of the gas present.

$$V \propto n \quad \text{or} \quad V = kn$$

Consider the reaction:



Chemistry 121: Topic 5 - The Gaseous State

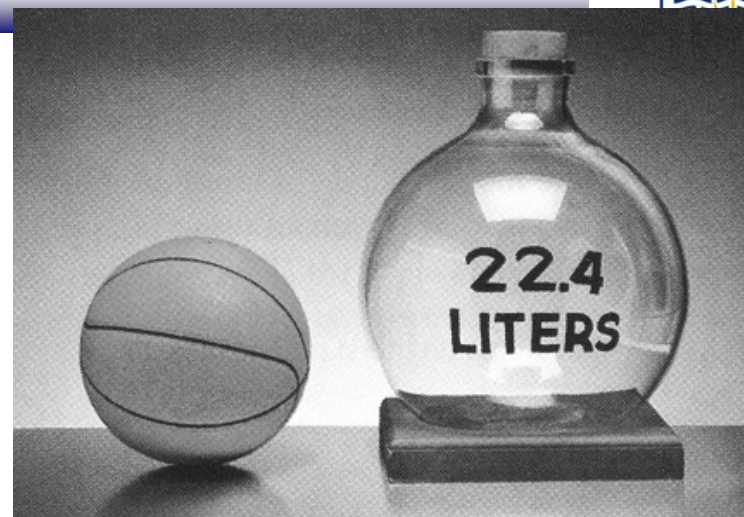
The Ideal Gas Equation:

Obtained by combining;

Boyle's Law; $P \propto \frac{1}{V}$

Charles Law; $P \propto T$

Avogadro's Law; $V \propto n$



$PV = nRT$ **Where;** R is a proportionality Constant called the gas constant

$$R = 0.082057 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}$$

The ideal gas equation describes the relationship among the variables P, V, T & n

An **ideal gas** is a hypothetical gas whose pressure-volume-temperature behavior can be completely accounted for by the ideal gas equation.

The conditions of 0°C and 1 atm are called the **standard temperature and pressure (STP)**.

At **STP** 1 mole of an ideal gas occupies a volume of 22.414 L

Chemistry 121: Topic 5 - The Gaseous State

Examples:

Example 5.5 Sulfur hexafluoride (SF_6) is a colorless, odorless, very unreactive gas. Calculate the pressure (in atm) exerted by 1.82 moles of the gas in a steel vessel of volume 5.43 L at 69.5°C .

Reasoning and Solution This problem provides information about the number of moles, volume, and temperature of a gas, but no change in any of the quantities occurs. Therefore, to calculate the pressure we can use the ideal gas equation, which can be rearranged to give

$$\begin{aligned}P &= \frac{nRT}{V} \\&= \frac{(1.82 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(69.5 + 273) \text{ K}}{5.43 \text{ L}} \\&= 9.42 \text{ atm}\end{aligned}$$

Example 5.6 Calculate the volume (in liters) occupied by 7.40 g of NH_3 at STP.

Reasoning and Solution Recognizing that 1 mole of an ideal gas occupies 22.41 L at STP, we write

$$\begin{aligned}V &= 7.40 \text{ g NH}_3 \times \frac{1 \text{ mol NH}_3}{17.03 \text{ g NH}_3} \times \frac{22.41 \text{ L}}{1 \text{ mol NH}_3} \\&= 9.74 \text{ L}\end{aligned}$$

Chemistry 121: Topic 5 - The Gaseous State



Useful Variations of the ideal gas law;

$$R = \frac{P_1 V_1}{n_1 T_1}$$

$$R = \frac{P_2 V_2}{n_2 T_2}$$

In other words;

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

if $n_1 = n_2$

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

For Density:

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

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

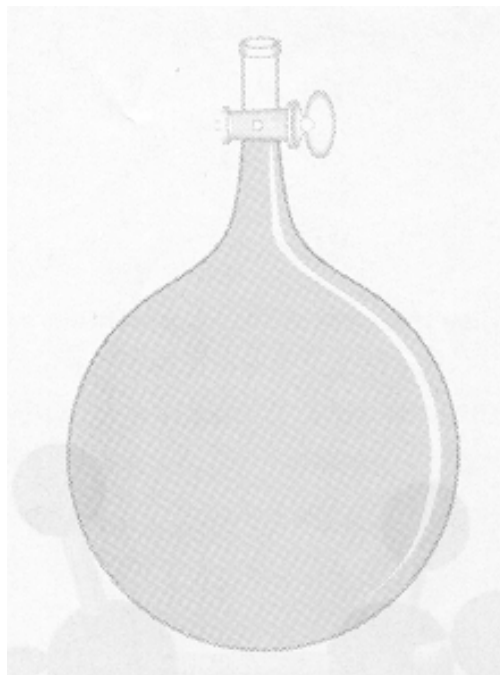
where; m = mass
 M = Molar mass

$$d = \frac{m}{V} = \frac{P M}{RT}$$

Express gas densities as g/L

Chemistry 121: Topic 5 - The Gaseous State

Molar Mass Relationship: Obtained by rearranging gas equation for density:



$$d = \frac{m}{V} = \frac{P M}{RT}$$

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

Example: A chemist has synthesized a greenish-yellow gaseous compound of chlorine and oxygen and finds that its density is 7.71 g/L at 36°C and 2.88 atm. Calculate the molar mass of the compound and determine its molecular formula.

$$M = \frac{d RT}{P} = \frac{7.71 \text{ g/L} (0.0821 \text{ L}\cdot\text{atm/K}\cdot\text{mol})(309\text{K})}{2.88 \text{ atm}} = 67.9 \text{ g/mol}$$

$$\begin{aligned} x (\text{Molar mass Cl}) + y (\text{Molar mass O}) &= 67.9 \text{ g/mol} \\ x (35.45 \text{ g/mol}) + y (16.00 \text{ g/mol}) &= 67.9 \text{ g/mol} \end{aligned}$$

If $x = 1$ and $y = 2$ then $67.45 \text{ g/mol} \therefore \text{ClO}_2$

Chemistry 121: Topic 5 - The Gaseous State



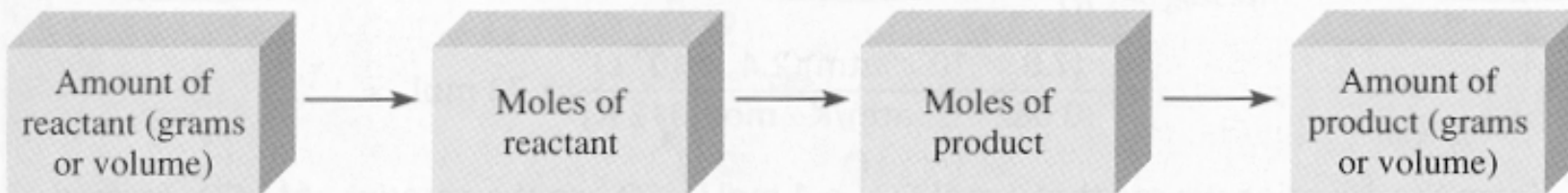
Gas Stoichiometry:

Example 5.12 Calculate the volume of O_2 (in liters) at STP required for the complete combustion of 2.64 L of acetylene (C_2H_2) at STP:

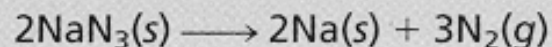


Reasoning and Solution Because both C_2H_2 and O_2 are gases measured at the same temperature and pressure, according to Avogadro's law their reacting volumes are related to their coefficients in the balanced equation; that is, 2 L of C_2H_2 react with 5 L of O_2 . Knowing this ratio we can calculate the volume (in liters) of O_2 that will react with 2.64 L of C_2H_2 .

$$\begin{aligned}\text{volume of } O_2 &= 2.64 \text{ L } C_2H_2 \times \frac{5 \text{ L } O_2}{2 \text{ L } C_2H_2} \\ &= 6.60 \text{ L } O_2\end{aligned}$$



Example 5.13 Sodium azide (NaN_3) is used in some automobile air bags. The impact of a collision triggers the decomposition of NaN_3 as follows:



The nitrogen gas produced quickly inflates the bag between the driver and the windshield. Calculate the volume of N_2 generated at 80°C and 823 mmHg by the decomposition of 60.0 g of NaN_3 .

Reasoning and Solution The problem requires two steps. First, we calculate the number of moles of N_2 generated from the decomposition of 60.0 g of NaN_3 . Next we calculate the volume of the N_2 gas at the given temperature and pressure.

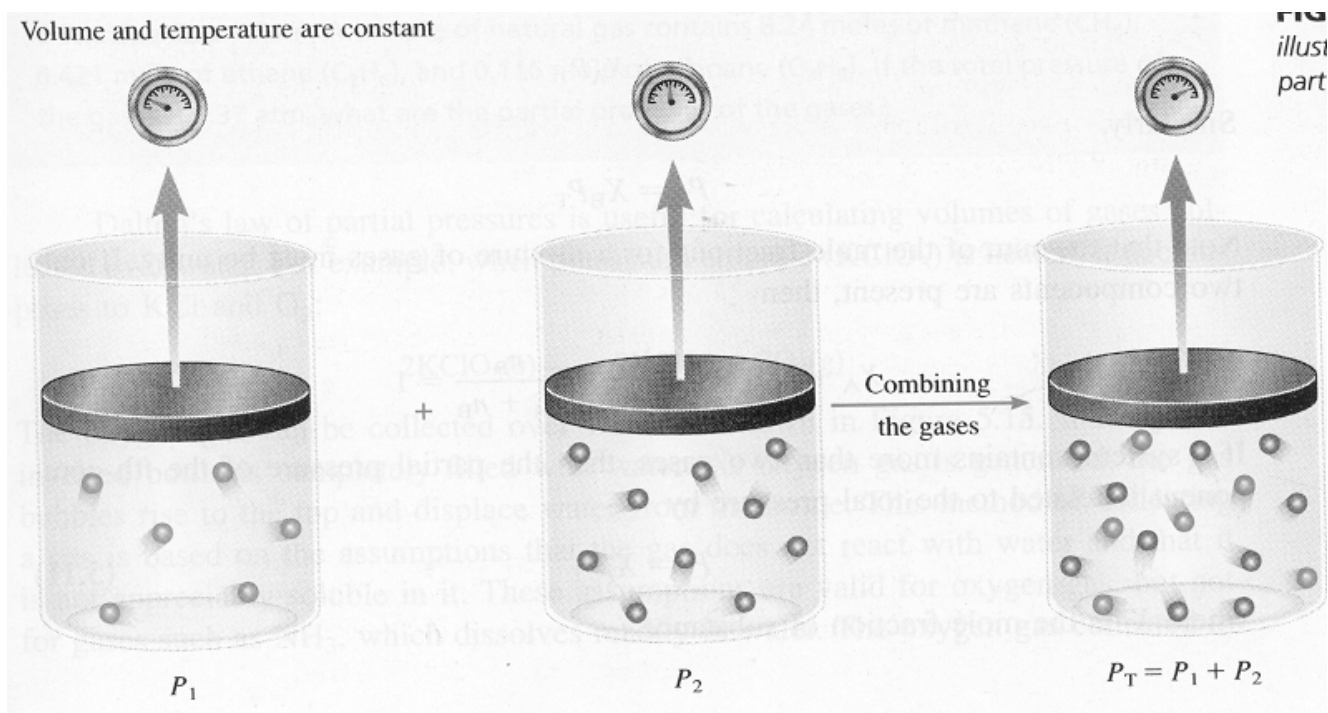
$$\begin{aligned}\text{moles of N}_2 &= 60.0 \text{ g NaN}_3 \times \frac{1 \text{ mol NaN}_3}{65.02 \text{ g NaN}_3} \times \frac{3 \text{ mol N}_2}{2 \text{ mol NaN}_3} \\ &= 1.38 \text{ mol N}_2\end{aligned}$$

The volume of 1.38 moles of N_2 can be obtained by using the ideal gas equation:

$$\begin{aligned}V &= \frac{nRT}{P} = \frac{(1.38 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(80 + 273) \text{ K}}{(823/760) \text{ atm}} \\ &= 36.9 \text{ L}\end{aligned}$$

Chemistry 121: Topic 5 - The Gaseous State

Dalton's Law of Partial Pressures: The total pressure of a mixture of gases is the sum of the pressures that each gas would exert if it were present alone.



Mole Fraction: A dimensionless quantity that expresses the ratio of the number of moles of one component to the total number of moles present.

$$X_A = \frac{P_A}{P_T} = \frac{(n_A RT)/V}{((n_A + n_B) RT)/V} = \frac{n_A}{n_A + n_B}$$

➤ $X_A + X_B = 1$

➤ $P_A = X_A P_T$

➤ $P_i = X_i P_T$

Chemistry 121: Topic 5 - The Gaseous State

Example:

Example 5.15 A mixture of gases contains 4.46 moles of neon (Ne), 0.74 mole of argon (Ar), and 2.15 moles of xenon (Xe). Calculate the partial pressures of the gases if the total pressure is 2.00 atm at a certain temperature.

Reasoning and Solution To calculate the partial pressures, we apply Dalton's law. First, we determine the mole fraction of Ne as follows

$$X_{\text{Ne}} = \frac{n_{\text{Ne}}}{n_{\text{Ne}} + n_{\text{Ar}} + n_{\text{Xe}}} = \frac{4.46 \text{ mol}}{4.46 \text{ mol} + 0.74 \text{ mol} + 2.15 \text{ mol}} = 0.607$$

From Equation (5.11)

$$\begin{aligned} P_{\text{Ne}} &= X_{\text{Ne}} P_{\text{T}} \\ &= 0.607 \times 2.00 \text{ atm} \\ &= 1.21 \text{ atm} \end{aligned}$$

Similarly,

$$\begin{aligned} P_{\text{Ar}} &= 0.10 \times 2.00 \text{ atm} \\ &= 0.20 \text{ atm} \end{aligned}$$

and

$$\begin{aligned} P_{\text{Xe}} &= 0.293 \times 2.00 \text{ atm} \\ &= 0.586 \text{ atm} \end{aligned}$$

Comment To check the correctness of the answer, make sure that the sum of the partial pressures is equal to the given total pressure; that is, $(1.21 + 0.20 + 0.586) \text{ atm} = 2.0 \text{ atm}$.

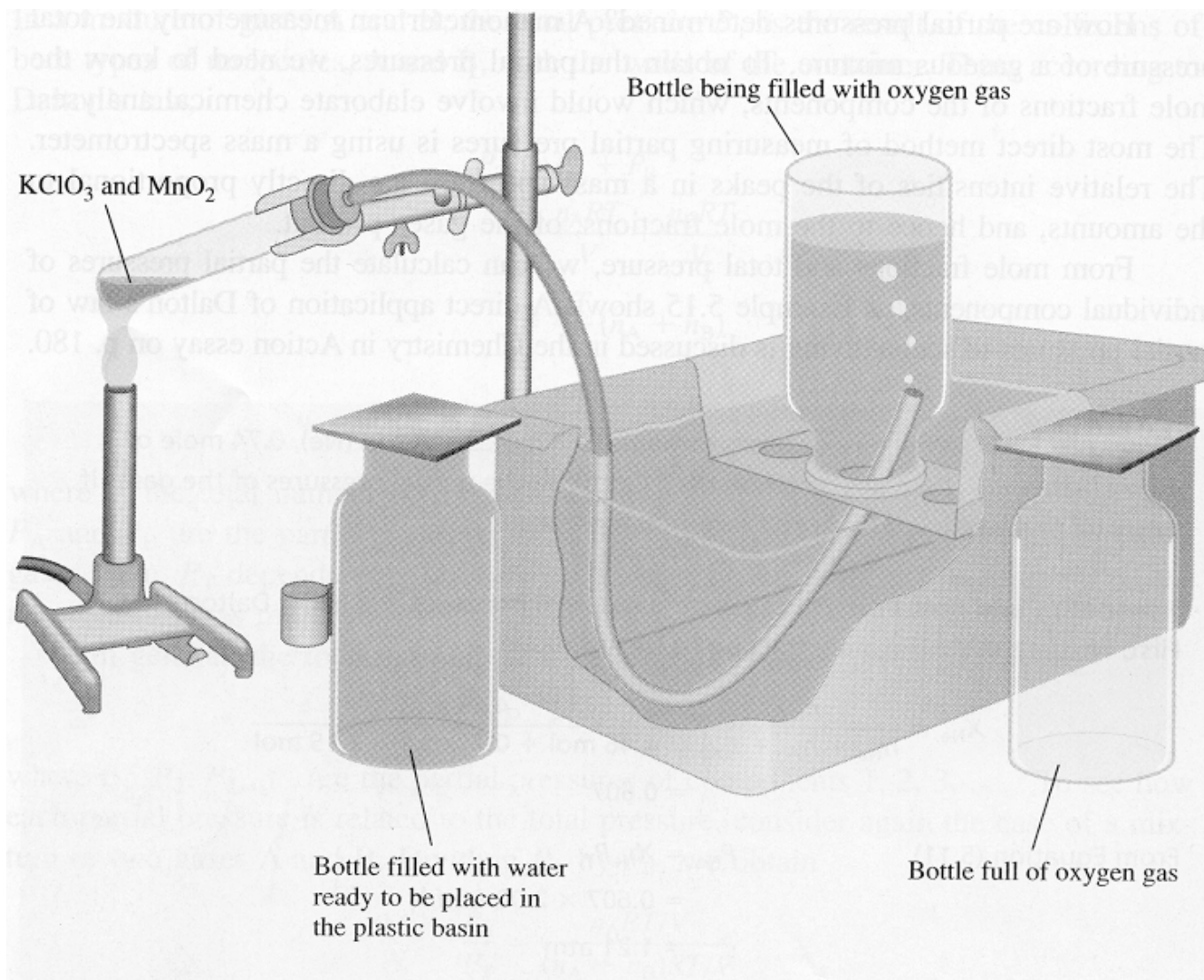
Chemistry 121: Topic 5 - The Gaseous State



Example: If 250 mL of gas is collected at 780 mm Hg and 25°C determine the number of grams of O_2 produced by the reaction.

Table 5.3 Pressure of Water Vapor at Various Temperatures

Temperature (°C)	Water Vapor Pressure (mmHg)
0	4.58
5	6.54
10	9.21
15	12.79
20	17.54
25	23.76
30	31.82
35	42.18
40	55.32
45	71.88
50	92.51
55	118.04
60	149.38
65	187.54
70	233.7
75	289.1
80	355.1
85	433.6
90	525.76
95	633.90
100	760.00



Chemistry 121: Topic 5 - The Gaseous State



Kinetic Molecular Theory of Gases:

Assumptions:

- Gas is composed of molecules, separated by distances far greater than their own dimensions. Molecules effectively "points" with mass negligible volume
- Gas molecules are in constant random motion, and they frequently collide. Collisions among molecules are perfectly elastic, with the total energy of all the molecules in a system remains the same.
- Gas molecules exert neither attractive nor repulsive forces on one another.
- The average kinetic energy of the molecules is proportional to the temperature in Kelvin's. Any two gases at the same temperature will have the same average kinetic energy. The average kinetic energy of a molecule is given by;

$$KE = \frac{1}{2} m u^2$$

Where; KE is the average Kinetic Energy;
 u^2 is the mean square speed (ave. all molecules)

$$\therefore \quad KE \propto T \quad : \quad \frac{1}{2} m u^2 \propto T \quad : \quad \frac{1}{2} m u^2 = C T$$

Chemistry 121: Topic 5 - The Gaseous State



Use of Kinetic Theory to Explain Gas Properties:

Compressibility of Gases: Since molecules in the gas phase are separated by large distances (assumption 1), gases can be compressed easily to occupy less volume.

Boyle's Law: The pressure exerted by a gas results from the impact of its molecules on the walls of the container. The collision rate, or the number of molecular collisions with the walls per second, is proportional to the number density (that is, number of molecules per unit volume) of the gas. Decreasing the volume of a given amount of gas increases its number density and hence its collision rate.

Charles's Law: Because the average kinetic energy of gas molecules is proportional to the sample's absolute temperature (assumption 4), raising the temperature increases the average kinetic energy. Consequently, molecules will collide with the walls of the container more frequently and with greater impact if the gas is heated, and thus the pressure increases.

Chemistry 121: Topic 5 - The Gaseous State



Use of Kinetic Theory to Explain Gas Properties:

Avogadro's Law: We have shown that the pressure of a gas is directly proportional to both the density and the temperature of the gas. Since the mass of the gas is directly proportional to the number of moles (n) of the gas, Therefore;

$$P \propto (n/V) T$$

Dalton's Law of Partial Pressures: If molecules do not attract or repel one another (assumption 3), then the pressure: exerted by one type of molecule is unaffected by the presence of another gas. Consequently, the total pressure is given by the sum of individual gas pressures.

Chemistry 121: Topic 5 - The Gaseous State



Example: If 250 mL of gas is collected at 780 mm Hg and 25°C; determine the number of grams of O₂ produced by the reaction. (see previous overhead #14)

$$@ 25^{\circ}\text{C } P_{\text{H}_2\text{O}} = 23.8 \text{ mm Hg} \quad \text{and} \quad P_{\text{total}} = P_{\text{O}_2} + P_{\text{H}_2\text{O}}$$

$$\therefore P_{\text{O}_2} = 760 \text{ mm Hg} - 23.8 \text{ mm Hg} = 736.2 \text{ mm Hg}$$

$$\frac{736.2 \text{ mm Hg}}{760 \text{ mm Hg} / \text{atm}} = 0.969 \text{ atm}$$

$$PV = nRT \quad (0.969 \text{ atm})(0.250 \text{ L}) = n(0.0821 \text{ L} \cdot \text{atm} / \text{K} \cdot \text{mol})(25 + 273.15 \text{ K})$$

$$n = \frac{(0.969 \text{ atm})(0.250 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm} / \text{K} \cdot \text{mol})(298.15 \text{ K})}$$

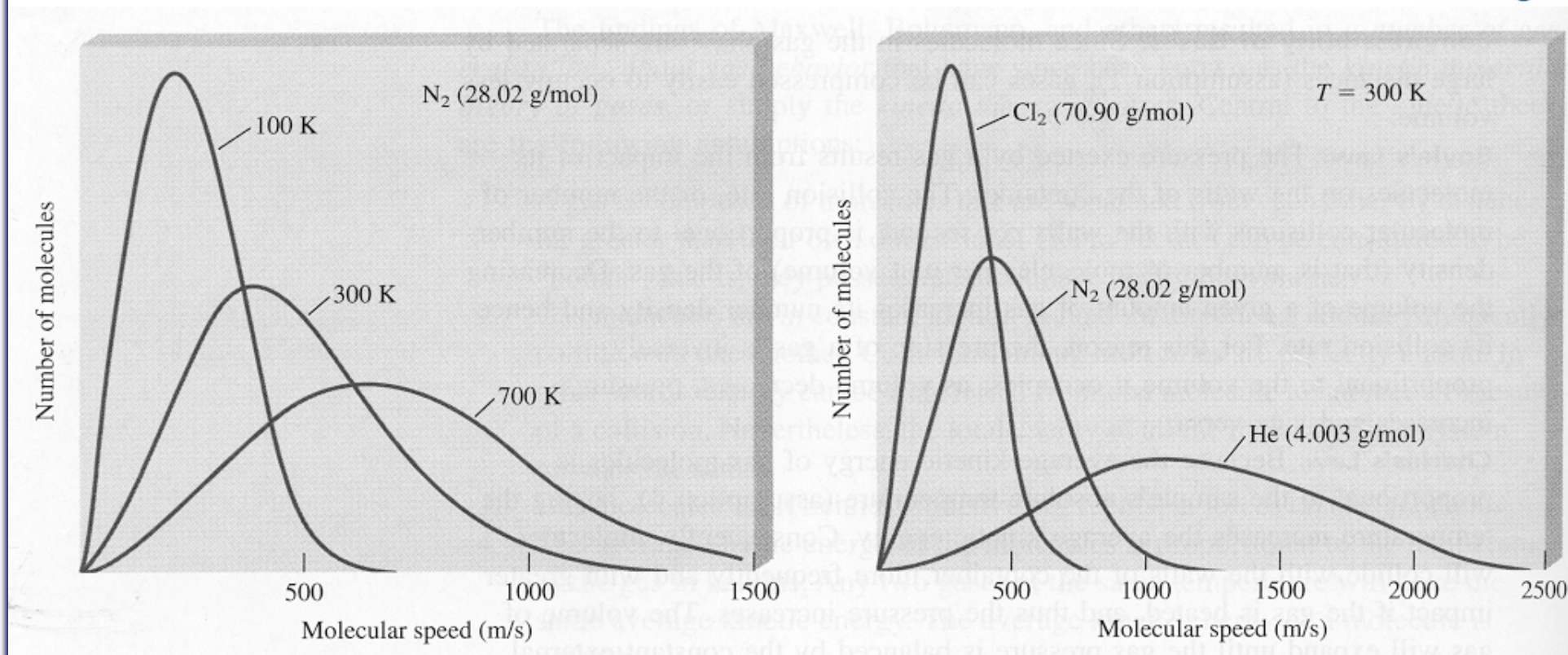
$$n = 9.90 \times 10^{-3} \text{ mol}$$

$$9.90 \times 10^{-3} \text{ mol} \times 32.00 \text{ g/mol} = 0.317 \text{ g O}_2$$

Chemistry 121: Topic 5 - The Gaseous State

Distribution of Molecular Speeds:

$$\frac{1}{2} m u^2 = (\text{Constant}) T$$



From Kinetic theory it can be shown that the total Kinetic Energy of one mole of any gas is $\frac{3}{2} RT$.

Chemistry 121: Topic 5 - The Gaseous State



Root-mean-square (u_{rms}) speed (u_{rms}) or Average Molecular Speed:

Knowing the total KE, the number of Particles (N_A) and the average KE

$$N_A \left(\frac{1}{2} m u^2 \right) = \frac{3}{2} RT \quad \text{and} \quad N_A m = M$$

$$u^2 = \frac{3RT}{M} \quad \sqrt{u^2} = \sqrt{\frac{3RT}{M}} \quad \sqrt{u^2} = u_{rms}$$

Because of the relationships between u_{rms} and molecular weight (M) the heavier the gas, the slower the molecules move.

R can be converted to energy terms as well

$$R = (0.0821 \text{ L} \cdot \text{atm} / \text{K} \cdot \text{mol}) \times (1 \times 10^{-3} \text{ m}^3 / \text{L}) \times (101,325 \frac{\text{N m}^2}{\text{atm}})$$

$$R = 8.314 \frac{\text{N m}}{\text{K mol}} = 8.314 \text{ J} / \text{K} \cdot \text{mol}$$

If this value for R is used with Molar weight in kg/mol ; u_{rms} in m/sec can be determined.

Chemistry 121: Topic 5 - The Gaseous State

Example 5.17 Calculate the root-mean-square speeds of helium atoms and nitrogen molecules in m/s at 25°C.

Reasoning and Solution We need Equation (5.13) to calculate the root-mean-square speeds. Note that because R has the units $\text{J/K} \cdot \text{mol}$, the molar mass must be expressed as kg/mol . Thus for He the molar mass should be $4.003 \times 10^{-3} \text{ kg/mol}$, not 4.003 g/mol .

$$\begin{aligned}u_{\text{rms}} &= \sqrt{\frac{3RT}{\mathcal{M}}} \\&= \sqrt{\frac{3(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K})}{4.003 \times 10^{-3} \text{ kg/mol}}} \\&= \sqrt{1.86 \times 10^6 \text{ J/kg}}\end{aligned}$$

Using the conversion factor,

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

we get

$$\begin{aligned}u_{\text{rms}} &= \sqrt{1.86 \times 10^6 \text{ kg m}^2/\text{kg} \cdot \text{s}^2} \\&= \sqrt{1.86 \times 10^6 \text{ m}^2/\text{s}^2} \\&= 1.36 \times 10^3 \text{ m/s}\end{aligned}$$

The procedure is the same for N_2 , which has a molar mass of 28.02 g/mol , or $2.802 \times 10^{-2} \text{ kg/mol}$:

$$\begin{aligned}u_{\text{rms}} &= \sqrt{\frac{3(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K})}{2.802 \times 10^{-2} \text{ kg/mol}}} \\&= \sqrt{2.65 \times 10^5 \text{ m}^2/\text{s}^2} \\&= 515 \text{ m/s}\end{aligned}$$

Chemistry 121: Topic 5 - The Gaseous State



Effusion and Diffusion:

Diffusion is the term used to describe the mixing of gases. The rate of diffusion is the rate of the mixing of gases.

Effusion is the term used to describe the passage of a gas through a tiny orifice into an evacuated chamber. The rate of effusion measures the rate at which the gas is transferred into the chamber.

Thomas Graham found experimentally that the rate of effusion of a gas is inversely proportional to the square root of the mass of its particles.

$$\frac{\text{Rate of Effusion of Gas 1}}{\text{Rate of Effusion of Gas 2}} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

Deviation from Ideal Behavior:

The assumptions of the gas laws and the kinetic theory describe an ideal and unobtainable case.

If a gas is ideal one mole of the gas would behave such that the relationship:

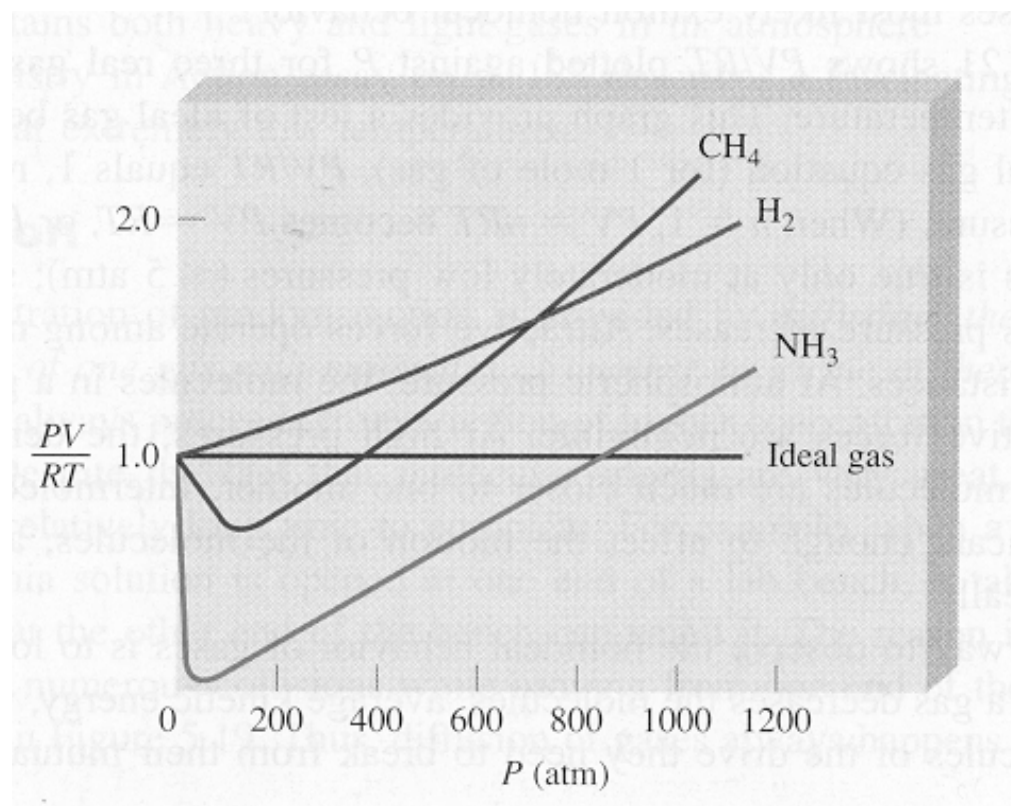
$$1 = \frac{PV}{RT} \quad \text{is always valid. However, in reality we get;}$$

To account for the variation
van der Waals suggested a correction
factor;

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

Where; a is a constant
 n is the # moles
 V is the Volume

This correction term corrects for
intermolecular attraction.



Chemistry 121: Topic 5 - The Gaseous State

van der Waals Equation;

In addition to the correction for the attractive forces (effecting the pressure)

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

The gas molecules also take up a finite volume and that must be taken into account as well, when this is done the net equation becomes;

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

Note:

- a indicates how strongly molecules attract each other
- the smallest a is for Helium
- Generally larger the molecule larger b, however that is not absolute.

Table 5.4 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 ₂	0.244	0.0266
N ₂	1.39	0.0391
O ₂	1.36	0.0318
Cl ₂	6.49	0.0562
CO ₂	3.59	0.0427
CH ₄	2.25	0.0428
CCl ₄	20.4	0.138
NH ₃	4.17	0.0371
H ₂ O	5.46	0.0305