Chapter 5: Gases

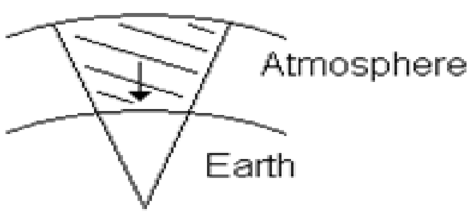
Sections 5.1 - 5.2: Pressure Measurements in Gases

The physical state of a gas is characterized by its pressure (P), its temperature (T), its volume (V) and the amount of matter (moles). Remember that in contrast with liquids and solids, gases completely fill the space of their container and gases are highly compressible.

Pressure is defined as force per unit area.

$$\text{Pressure (P)} = \frac{\text{Force (F)}}{\text{Area (A)}}$$

$$\text{Atmospheric Pressure} = \frac{\text{Force from mass of air pulled toward Earth's center by gravity}}{\text{Area}}$$



As one changes altitude, the mass of air above you decreases; thus the pressure decreases as the altitude increases.

Units of Pressure:

- Atmosphere = atm
- Millimeters of mercury = mm Hg
- Torr = Torr
- Pascal = Pa (SI unit: 1 Pa = 1 Newton/m^2)

Conversions between units:

1 atm = 760 mm Hg = 76 cm Hg = 760 Torr = 101325 Pa

Generally, we will use the approximation: 1 atm = 760 Torr $\cong$ 101.3 kPa

The instrument used to measure the atmospheric pressure is called the barometer.

Example: Convert 432 mm Hg to atmospheres and kilopascals.

$$\text{Thus, } 432\ \text{mm Hg} \times \frac{1\ \text{atm}}{760\ \text{mm Hg}} = 0.568\ \text{atm}$$

(Note: The result has three significant figures since 760 and 1 are exact numbers)

$$\text{and } 0.568\ \text{atm} \times \frac{101.3\ \text{kPa}}{1\ \text{atm}} = 57.6\ \text{kPa}$$

Example: A gas pressure is measured as 52 Torr. Convert this to atmospheres and pascals.

$$52\ \text{Torr} \times \frac{1\ \text{atm}}{760\ \text{Torr}} = 0.068\ \text{atm}$$

$$0.068\ \text{atm} \times \frac{101.3\ \text{kPa}}{1\ \text{atm}} \times \frac{1000\ \text{Pa}}{1\ \text{kPa}} = 6931\ \text{Pa or } 6.9 \times 10^3\ \text{Pa}$$

In Section 5.2, practice the Interactive Problems.

Sections 5.3 - 5.4: Boyle's Law

"At constant Temperature (T), the Volume (V) of a gas sample varies inversely with Pressure (P)". This result was first reported by Robert Boyle in 1661. Mathematically, **Boyle's law** is expressed as:

$$P \propto \frac{1}{V} \qquad \text{or} \qquad V \propto \frac{1}{P} \qquad \text{at constant temperature and number of moles}$$

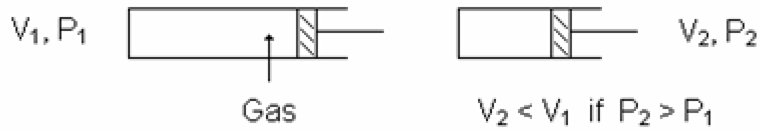
$$\text{or} \qquad P \times V = \text{Constant}$$

As the gas is compressed, the molecules are confined to a smaller volume.

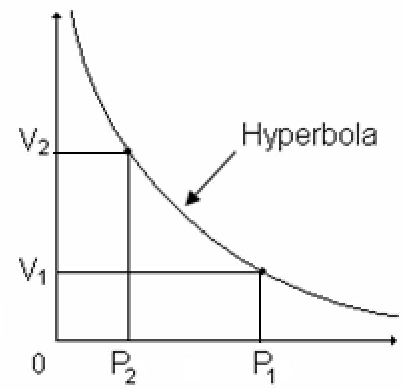
Consider two sets of conditions: 1. Initial and 2. Final

One can say that if T and n (i.e. number of moles) are constant, then a change in pressure from P_1 to P_2 leads to a change in volume from V_1 to V_2, such that

$$P_2 \times V_2 = P_1 \times V_1 = \text{Constant}$$



At a fixed temperature T and # moles of gas, changing the pressure P leads to change in volume V, such that the point (V, P) describes a hyperbola.



Example 1: A gas sample occupies 180 L at 1.00 atm. Calculate the pressure needed to compress the gas to 50 L at the same temperature.

P_1 = 1.00 atm
P_2 = to be calculated
V_1 = 180 L
V_2 = 50.0 L

$$P_2V_2 = P_1V_1$$

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

$$P_2 = 1.00 \text{ atm} \times \frac{180 \text{ L}}{50.0 \text{ L}} = 3.6 \text{ atm}$$

Note: As the Pressure increases, the Volume decreases at constant Temperature.

Example 2: A 2.00 L of H_2 gas is compressed from 320. kPa to 5.00 atm. Calculate the final volume.

1 atm = 760 mm Hg = 760 Torr = 101.3 kPa

$$P_1 = 320\,\text{kPa} \times \frac{1\,\text{atm}}{101.3\,\text{kPa}} = 3.16\,\text{atm}$$

P_1 = 3.16 atm
P_2 = 5.00 atm
V_1 = 2.00 L
V_2 = To be calculated

$$3.16\ \text{atm} \times 2.00\ \text{L} = 5.00\ \text{atm} \times V_2$$

$$V_2 = \frac{3.16\,\text{atm} \times 2.00\,\text{L}}{5.00\,\text{atm}} = 1.26\,\text{L}$$

In Section 5.4, practice the Interactive Problems.

Sections 5.5 - 5.6: Charles's Law

"At constant Pressure (P), the Volume (V) of a gas sample is directly proportional to the absolute Temperature (T)". This observation was first made by Jacques Alexandre Charles in 1787.Mathematically, **Charles's law** is expressed as:

$V \propto T$ at constant Pressure (P) and number of moles

$$\text{or} \quad \frac{V}{T} = \text{Constant} \quad .$$

Note: Doubling the absolute Temperature (T) of a gas doubles its Volume (V).

If the temperature of a gas is changed from T_1 to T_2, the volume of this gas changes from V_1 to V_2, such that:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = \text{Constant}$$

Example 1: At 20.0 deg.C a balloon filled with helium gas occupies a volume of 262 L. Calculate the volume of helium gas if the temperature was to drop to –10.00 deg.C.

V_1 = 262 L
V_2 =To be calculated
T_1 = 293.15 K
T_2 = 263.15 K

$$\frac{262\ \text{L}}{293.15\,\text{K}} = \frac{V_2}{263.15\,\text{K}}$$

$$V_2 = \frac{262\,\text{L} \times 263.15\,\text{K}}{293.15\,\text{K}} = 235\,\text{L}$$

Example 2: A sample of oxygen gas occupies a volume of 2.54 L at 1.00 atm and 22.00 deg.C. Calculate the temperature of the oxygen gas in deg.C if the volume is decreased to 1.24 L at 1.00 atm.

V_1 = 2.54 L	V_2 = 1.24 L
T_1 = 295.15 K	T_2 = To be calculated
P_1 = 1 atm	P_2 = 1 atm

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

$$T_2 = 295.15\ \text{K} \times \frac{1.24\,\text{L}}{2.54\,\text{L}}$$

T_2 = 144 K = -129 ^{o}C

In Section 5.6, practice the Interactive Problems.

Sections 5.7 - 5.8: Gay-Lussac's Law

"At constant Volume (V), the Pressure (P) of a gas sample is directly proportional to the absolute Temperature (T)". This observation was first reported by Gay-Lussac in 1787. Mathematically, Gay-Lussac's law is expressed as:

$P \propto T$ at constant Volume (V) and number of moles

$$\text{or } \frac{P}{T} = \text{Constant}$$

If the temperature of a gas is changed from T_1 to T_2, then the pressure in the gas is changed from P_1 to P_2 such that:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} = \text{Constant if V and n are held constant}$$

Example 1: At constant volume, a certain gas has a pressure of 600. Torr at 85.00 deg.C. Calculate the pressure in Torr at 170.00 deg.C.

P_1 = 600. Torr
P_2 = To be calculated
T_1 = 358.15 K
T_2 = 443.15 K

$$\frac{600.\text{ Torr}}{358.15\text{ K}} = \frac{P_2}{443.15\text{ K}}$$

$$P_2 = \frac{600.\text{ Torr x } 443.15\text{ K}}{358.15\text{ K}} = 742\text{ Torr}$$

Note: Doubling the absolute Temperature doubles the Pressure of a gas at constant Volume.

Example 2: A 250. mL can filled with gas at 25.00 deg.C and 1.10 atm was thrown into an incinerator. When the temperature of the can reached 605.00 deg.C, the can exploded. Calculate the pressure (in Torr) in the can just before it exploded.

P_1 = 1.10 atm
T_1 = 273.15 + 25.00 = 298.15 K
V_1 = 250. mL
P_2 = To be calculated
V_2 = 250. mL
T_2 = 605.00 ^{o}C = 878.15 K

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \Rightarrow P_2 = P_1 \frac{T_2}{T_1} = 1.1\text{ atm x } \frac{878.15\text{K}}{298.15\text{ K}}$$

P_2 = 3.24 atm

$$\text{In Torr,} \qquad P_2 = 3.24 \text{ atm} \times \frac{760 \text{ Torr}}{1 \text{ atm}}$$

$$P_2 = 2460 \text{ Torr}$$

In Section 5.8, practice the Interactive Problems.

Sections 5.9 - 5.10: Combined Gas Law

Boyle's Law states	$P \propto \frac{1}{V}$	at constant T and n.
Charles's Law states	$V \propto T$	at constant P and n.
Gay-Lussac's Law states	$P \propto T$	at constant V and n.

Combining these three laws, we get:

$$PV \propto T \qquad \text{at constant n}$$

or

$$\frac{PV}{T} = \text{Constant} \qquad \text{when n is constant}$$

This means that if a gas occupies a volume V_1 at temperature T_1 under a pressure P_1, then the same sample of gas (same n) occupies a volume V_2 at temperature T_2 under a pressure P_2, such that:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} = \text{Constant}$$

This equation is called the **Combined Gas Law**.

Example 1: A mole of gas at 0 deg.C and 760 Torr occupies 22.4 L. Calculate the volume in liters at 20 ^{o}C and 960 Torr.

P_1 = 760 Torr
P_2 = 960 Torr
V_1 = 22.4 L
V_2 = To be calculated
T_1 = 273 K
T_2 = 293 K

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

$$V_2 = 22.4 \text{ L} \times \frac{760 \text{ Torr}}{960 \text{ Torr}} \times \frac{293\text{K}}{273\text{K}}$$

$$V_2 = 19 \text{ L}$$

In Section 5.10, practice the Interactive Problems.

Sections 5.11 - 5.12: The Ideal Gas Law

According to Boyle's Law $P \propto \frac{1}{V}$ at constant T

According to Charles Law $V \propto T$ at constant P

Combine these two laws and we get: $V \propto \frac{T}{P}$

The Volume (V) of gas is also directly proportional to the amount of gas.
The amount of gas is expressed as moles of gas "n".

$$V \propto \frac{nT}{P}$$

$$V = \text{constant} \times \frac{nT}{P}$$

The constant is called the gas constant and is represented by the symbol R.

$$V = R\frac{nT}{P}$$

$$PV = nRT$$

This equation is called the **Ideal Gas Law**.

P = Pressure expressed in atmospheres (atm)
V = Volume expressed in liters (L)
n = moles expressed in mol.
R = gas constant, 0.0821 $L.atm.mol^{-1}.K^{-1}$
T = Absolute temperature expressed in kelvin (K)

R, the gas constant is expressed in different units. In ideal gas law applications, with pressure given in atmosphere and volume in liters, always use R = 0.0821 $L.atm.mol^{-1}.K^{-1}$.

Example 1: The molecular formula of a certain gas is $C_2F_4H_2$. If 3.50 g of this gas is placed in a container having a volume of 500 mL at 10 ^oC, calculate the pressure in atmospheres.

P = To be calculated

V = 500 mL = 0.500 L

R = 0.0821 $L.atm.mol^{-1}.K^{-1}$

T = 10 ^oC = 283 K

$$n = \frac{3.50\ g}{102.0\ g/mol} = 0.0343\ mol$$

PV = nRT

$$P = \frac{0.0343\ mol\ x\ 0.0821\ L.atm.mol^{-1}.K^{-1}\ x\ 283\ K}{0.500\ L}$$

P = 1.60 atm

Example 2: Determine the mass of gas (N_2) in 1.50 L of gas at 20 ^oC and 0.874 atm.

$$PV = nRT \quad \Rightarrow \quad n = \frac{PV}{RT}$$

P = 0.874 atm
V = 1.50 L
T = 293 K
n = To be calculated

$$n = \frac{0.874\ \text{atm}\ \times\ 1.50\ \text{L}}{0.0821\ \frac{\text{atm.L}}{\text{mol.K}} \times 293\,\text{K}} = 0.0545\,\text{mol}$$

mass = moles × molar mass = 0.0545 mol × 28.0 g/mol = 1.53 g

In Section 5.12, practice the Interactive Problems.

Sections 5.13 - 5.14: Avogadro's Law

"Any two gases having equal volumes at the same temperature and at the same pressure contain the same number of molecules."

One mole of gas contains Avogadro's number of molecules. Recall Avogadro's number, $N_A = 6.022 \times 10^{23}$

Volumes of gases are often compared at the **Standard Temperature and Pressure (STP)**. The Standard Temperature is 0 deg.C and the Standard Pressure is 1 atm. At STP, one mole of any gas occupies a volume of 22.4 L. The Standard Temperature and Pressure state or STP state is used to tabulate data on chemicals.

Avogadro's law says that: 1 mole of gas in the STP state occupies 22.4 L.

P = 1 atm n = 1 mole V = 22.4 L T = 273.15 K

$$P = \frac{nRT}{V} \qquad .$$

Avogadros law is the Ideal Gas Law for 1 mole at STP

Example 1: A 1.50 L sample of gas at 25.00 deg.C exerts a pressure of 0.874 atm. Calculate the number of moles of the gas sample at STP.

P_1 = 0.874 atm
P_2 = 1 atm
V_1 = 1.50 L
V_2 = To be calculated
T_1 = 298.15 K
T_2 = 273.15 K

$$\frac{0.874\ \text{atm}\ \times\ 1.50\ \text{L}}{298.15\ \text{K}} = \frac{1\text{atm}\ \times\ V_2}{273.15\ \text{K}}$$

$$V_2 = \frac{0.874\ \text{atm}\ \times\ 1.50\ \text{L}\ \times\ 273.15\ \text{K}}{298.15\ \text{K}\ \times\ 1\ \text{atm}} = 1.20\ \text{L}$$

From Avogadro's law, we know 1 mole of gas at STP occupies 22.4 L.

$$n = 1.20\ \text{L}\ \times\ \frac{1\ \text{mol}}{22.4\ \text{L}} = 0.0536\ \text{mol}$$

Example 2: Calculate the number of molecules in a 450 mL gas sample at -45.00 ^{o}C and 745 Torr.

P_1 = 745 Torr
P_2 = 760 Torr
V_1 = 0.450 L
V_2 = To be calculated
T_1 = 228.15 K
T_2 = 273.15 K

$$\frac{745\ \text{Torr}\ \times\ 0.450\ \text{L}}{228.15\ \text{K}} = \frac{760\ \text{Torr}\ \times\ V_2}{273.15\ \text{K}}$$

$$V_2 = \frac{745\ \text{Torr}\ \times\ 0.450\ \text{L}\ \times\ 273.15\ \text{K}}{228.15\ \text{K}\ \times\ 760\ \text{Torr}} = 0.528\ \text{L}$$

From Avogadro's law, we know 1 mole of gas at STP occupies 22.4 L.

$$\text{number of molecules} = 0.236\ \text{mol} \times \frac{6.022 \times 10^{23}\ \text{molecules}}{1\ \text{mol}}$$

number of molecules = 1.42 $\times$ 10^{22} molecules

Another way to solve this problem which is not covered on the DVD is:

P_1 = 745 Torr
V_1 = 0.450 L
T_1 = - 45.00 ^{o}C = 228.15 K

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

$$n = \frac{745 \text{ Torr} \times \dfrac{1 \text{ atm}}{760 \text{ Torr}} \times 0.450 \text{ L}}{0.0821 \dfrac{\text{L.atm}}{\text{K.mol}} \times 228.15 \text{ K}} = 0.0236 \text{ mol}$$

$$n = 0.0236 \text{ mol} \times \frac{6.022 \times 10^{23} \text{ molecules}}{1 \text{ mol molecules}} = 1.42 \times 10^{22} \text{ molecules}$$

In Section 5.14, practice the Interactive Problems.

Sections 5.15 - 5.16: Gas Density

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

The volume of solids and liquids does not change "significantly" when the pressure is changed. Hence, their density does not change very much when the pressure is changed.

In contrast, gases are very compressible (that is, their volume changes "significantly" when the applied pressure changes). Hence, the density of gases changes with pressure.

Now, we will see that we can use the Ideal Gas Law and the definition of density to obtain a new relation between P, d (density), R, T and M (molar mass).

$$PV = nRT \qquad\qquad P = \frac{n}{V} \times RT$$

$$\left.\begin{array}{l} \text{Density} = d = \dfrac{m \text{ (mass)}}{V} \\ m = n \times M \text{ (molar mass)} \end{array}\right\} \qquad d = \frac{n \times M}{V} \text{ or } \frac{n}{V} = \frac{d}{M}$$

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

or

$$d = \frac{P \times M}{R \times T}$$ is used to estimate the density of a specific gas at a given T and P.

This equation can be used to estimate the molar mass of a compound from knowledge of mass, pressure, volume and temperature.

For a given set of gases at a particular Pressure and Temperature P, R, and T are constant. Hence, density (d) is directly proportional to the molar mass of the gas.

$$d \propto \text{molar mass}$$

Thus, the higher the molar mass, the greater the density.

Example 1: Calculate the density of carbon dioxide gas at 125.00 ^{o}C and 714 Torr.

M = 44.0 g/mol
R = 0.0821 L.atm.mol^{-1}.K^{-1}
T = 125.00 ^{o}C = 398.15 K
P = 714 Torr = 0.939 atm

$$d = \frac{P \times M}{R \times T} = \frac{0.939\ \text{atm} \times 44.0\ \text{g.mol}^{-1}}{0.0821\ \frac{\text{L.atm}}{\text{K.mol}} \times 398.15\ \text{K}}$$

d = 1.26 g/L

Example 2: Calculate the molar mass of dry air if it has a density of 1.17 g/L at 22.00 ^{o}C and 745 Torr.

d = 1.17 g/L
R = 0.0821 L.atm. mol^{-1}.K^{-1}
T = 22.00 ^{o}C = 295.15 K
P = 745 Torr = 0.980 atm

$$M = \frac{dRT}{P} = \frac{1.17\ \frac{\text{g}}{\text{L}} \times 0.0821\ \frac{\text{L.atm}}{\text{K.mol}} \times 295.15\ \text{K}}{745\ \text{Torr} \times \frac{1\ \text{atm}}{760\ \text{Torr}}}$$

M = 28.9 g/mol

In Section 5.16, practice the Interactive Problems.

Sections 5.17 - 5.18: Stoichiometry of Gaseous Reactions

In a chemical reaction, gases are often reactants or products. Hence, understanding the properties of gases becomes very important. The important steps to remember while performing stoichiometric calculations are:

Step 1: Know how to write and balance a chemical equation.

Step 2: Convert the given amount of reactants or products to moles.

Step 3: Derive the mole ratio.

$$\text{mole ratio} = \frac{\text{moles desired}}{\text{moles given}}$$

Step 4: Multiply the mole ratio by the quantity of moles given (or calculated) in the problem. In gaseous reactions, use the Ideal Gas Law PV = nRT to calculate the property in question.

Note: In some examples, you may have to use PV = nRT first, to calculate “n” and then follow the four steps.

Example 1: Calculate the mass of hydrogen peroxide (H_2O_2) used to produce 2.00 L of O_2 gas at 25.00 ^oC and 1.00 atm according to the equation.

$$2\ H_2O_2 \rightarrow O_2 + 2\ H_2O$$

Use the ideal gas law to calculate the moles of oxygen.

P = 1.00 atm
V = 2.00 L
n = to be calculated
R = 0.0821 L.atm.mol^{-1}.K^{-1}
T = 298.15 K

$$n = \frac{P \times V}{R \times T} = \frac{1.00\ \text{atm} \times 2.00\,\text{L}}{0.0821\ \frac{\text{L.atm}}{\text{K.mol}} \times 298.15\,\text{K}} = 0.0817\,\text{mol}\,O_2$$

In order to calculate the number of moles of H_2O_2, use the four steps.

$$\frac{2\ \text{mol}\ H_2O_2}{1\ \text{mol}\ O_2} \times 0.0817\ \text{mol}\ O_2 = 0.1634\ \text{mol}\ H_2O_2$$

However, the problem asks for the mass of H_2O_2. Mass = moles x molar mass

Mass = 0.1634 mol x 34.0 g/mol = 5.56 g H_2O_2

Example 2: Calculate the volume of SO_2 gas produced at 25.00 ^oC and 1.00 atm by burning 20.0 g of S_8 oxygen.

$$S_{8\ (s)} + 8\ O_{2\ (g)} \rightarrow 8\ SO_{2\ (g)}$$

In order to calculate the number of moles of SO_2 use the four steps.

$$\text{moles } S_8 = \frac{20.0\ \text{g}}{256.8\ \text{g/mol}} = 0.0779\ \text{mol } S_8$$

$$\text{mole ratio} = \frac{8\ \text{mol}\ SO_2}{1\ \text{mol}\ S_8}\ \text{from the balanced reaction}$$

$$\frac{8\ \text{mol}\ SO_2}{1\ \text{mol}\ S_8} \times 0.0779\ \text{mol}\ S_8 = 0.623\ \text{mol}\ SO_2$$

P = 1.00 atm

V = to be calculated

n = 0.623 mol

T = 25.00 ^oC = 298.15 K

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

$$V = \frac{nRT}{P} = \frac{0.623\ \text{mol} \times 0.0821\ \frac{\text{L.atm}}{\text{K.mol}} \times 298.15\ \text{K}}{1.00\ \text{atm}}$$

V = 15.2 L

In Section 5.18, practice the Interactive Problems.

Sections 5.19 - 5.20: Partial Pressures in Gas Mixtures

Ideal Gas law also applies to gas mixtures. Each gas exerts <u>its own pressure</u>. This is called the partial pressure of that gas.

Consider a gas mixture containing gases A and B in a container of volume V at temperature T. For gases A and B, $P_A = n_ART/V$ and $P_B = n_BRT/V$

P_A is the partial pressure of component A.

P_B is the partial pressure of component B.

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

$$P_{Total} = (n_A + n_B)\,\frac{RT}{V} = \frac{n_ART}{V} + \frac{n_BRT}{V}$$

$$P_{Total} = P_A + P_B$$

This is the **Dalton's Law of Partial Pressures**. "In a mixture of gases, the total pressure is the sum of the partial pressures of the mixture's components."

Example 1: A 1.00 g sample of dry air consists of 0.77 g Nitrogen (N_2) and 0.23 g Oxygen (O_2). Calculate the partial pressure of O_2 and N_2 (in atm) assuming a volume of 1.00 L and temperature of 25.00 ^oC. Calculate the total pressure.

The ideal gas law requires the use of moles.

Transform mass to moles to calculate the partial pressure of N_2.

$$n_{N_2} = \frac{0.77\text{ g}}{28\text{ g/mol}} = 0.0275\text{ mol}$$

$$V = 1.00\text{ L}$$

$$T = 25.00\ ^oC = 298.15\text{ K}$$

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

$$P_{N_2} = \frac{0.0275\ \text{mol} \times 0.0821\ \frac{\text{L.atm}}{\text{K.mol}} \times 298.15\ \text{K}}{1.00\ \text{L}}$$

$$P_{N_2} = 0.67 \text{ atm}$$

Transform mass to moles to calculate the partial pressure of O_2.

$$n_{O_2} = \frac{0.23 \text{ g}}{32 \text{ g/mol}} = 0.00718 \text{ mol}$$

$$V = 1.00 \text{ L}$$

$$T = 25.00\ ^{o}C = 298.15 \text{ K}$$

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

$$P_{O_2} = \frac{0.00718 \text{ mol} \times 0.0821 \ \frac{\text{L.atm}}{\text{K.mol}} \times 298.15 \text{ K}}{1.00 \text{ L}}$$

$$P_{O_2} = 0.18 \text{ atm}$$

$$P_{Total} = 0.67 + 0.18 = 0.85 \text{ atm}$$

When a gas is collected by bubbling through water, it has vapor pressure associated with it. Dalton's law can be applied to the collected gas as:

$$P_{Total} = P_{gas} + P_{H_2O}$$

P_{H_2O} is the vapor pressure of liquid water. The "Table" on the DVD gives the values of water vapor pressure at different temperatures.

Example 2: 160 mL of hydrogen gas at 760. mm Hg is collected over water at 25 deg.C. Calculate the partial pressure of hydrogen gas.

P_{H_2O} = 23.76 mmHg (value obtained from the Table)

$$P_{Total} = 760. \text{ mmHg}$$

$$760. \text{ mm Hg} = P_{gas} + 23.76 \text{ mm Hg}$$

$$P_{gas} = 736 \text{ mm Hg}$$

In Section 5.20, practice the Interactive Problems.

Sections 5.21 - 5.22: Mole Fractions

Mole fraction is a quantity that is used to represent the composition of a mixture. We have already talked about molarity of a solute (moles of solute per liter of solution).

Mole fraction is defined by:

$$X_A = \text{mole fraction of component A in a mixture (A,B)} = \frac{n_A}{n_A + n_B}$$

$$X_A = \frac{n_A}{n_A + n_B} \quad \text{and} \quad X_B = \frac{n_B}{n_A + n_B}$$

$$X_A + X_B = 1 \qquad\qquad X_B = 1 - X_A$$

$$P_{Total} = n_{Total}\frac{RT}{V} = (n_A + n_B)\frac{RT}{V}$$

$$P_A = n_A\frac{RT}{V}$$

$$\frac{P_A}{P_{Total}} = \frac{n_A\frac{RT}{V}}{(n_A + n_B)\frac{RT}{V}} = \frac{n_A}{n_A + n_B}$$

$$\frac{P_A}{P_{Total}} = X_A$$

$$P_A = X_A P_{Total}$$

Example 1: Analysis of dry air, when the barometric pressure is 760 Torr, shows mole fractions of nitrogen and oxygen to be 0.781 and 0.219, respectively. Calculate the partial pressures of nitrogen and oxygen.

$$P_{Total} = 760 \text{ Torr} \qquad X_{N_2} = 0.781$$

$$P_{N_2} = 760 \text{ Torr} \times 0.781 = 594 \text{ Torr}$$

P_{Total} = 760 Torr X_{O_2} = 0.219

P_{O_2} = 760 Torr x 0.219 = 166 Torr

Verification: According to Dalton's Law $P_{Total} = P_{N_2} + P_{O_2}$

P_{Total} = 594 Torr + 166 Torr

P_{Total} = 760 Torr

Example 2: A gas mixture contains 3.0 mol N_2, and 2.0 mol O_2. Calculate the mole fraction of each component.

n_{Total} = 3.0 mol N_2 + 2.0 mol O_2

= 5.0 mol

$$X_{N_2} = \frac{3.0\text{ mol } N_2}{5.0\text{ mol}} = 0.60$$

$$X_{O_2} = \frac{2.0\text{ mol } O_2}{5.0\text{ mol}} = 0.40$$

Note: "In a gas mixture, the sum of mole fractions is always equal to one".
In this example: 0.60 + 0.40 = 1.00

In Section 5.22, practice the Interactive Problems.

Section 5.23: Kinetic Theory Postulates

All gases behave similarly as far as particle motion is concerned (PV = nRT). The ideal gas equation can be derived from first principles (Newton's laws) using the following assumptions or postulates.

Postulate #1

Gases consist of atoms or molecules in continuous, random motion. These atoms or molecules are called particles and they undergo frequent collisions with each other and with the walls of the container. Gas pressure results from collisions with the walls.

Postulate #2

Collisions between particles (atoms or molecules) are elastic. Therefore, there is no change in energy when a collision occurs and consequently, no kinetic energy is converted to heat. This is the reason why the temperature of an insulated gas does not change with time.

Postulate #3

Volume occupied by particles is negligible compared to the volume of the container (only true at ordinary temperature and pressure).

Postulate # 4

Attractive forces between particles have a negligible effect on the gas behavior (only true at ordinary temperature and pressure).

Postulate # 5

Average translational kinetic energy is directly proportional to the absolute temperature.

$$E_T \propto T \quad \text{or} \quad E_T = CT$$

Postulate #6

At a given temperature, all gas particles have the same average translational kinetic energy, E_T. Hence, the constant C in Postulate 5 has the same value for all gases.

Sections 5.24 - 5.25: Average Speed of Gas Particles

$E_T = ½\ mv^2$ Average Translational Kinetic Energy

m = mass of particle

v = average speed

$$E_T = \frac{1}{2} m v^2 = C\,T$$

$$v^2 = \frac{2CT}{m}$$

$$v = \sqrt{\frac{2CT}{m}} \quad \text{and} \quad C = \frac{3R}{2N_{avogadro}}$$

Note: $R = 8.31\ kg.m^2.s^{-2}.mol^{-1}.K^{-1}$!!!

$$v = \sqrt{\frac{3RT}{M}} \qquad M = m \times N_{avogadro}$$

MEMORIZE THIS EQUATION   molar mass   particle mass

$$v = \frac{1}{\sqrt{M}}$$

For two types of molecules A and B, there will be two average velocities v_A and v_B.

$$\frac{v_A}{v_B} = \sqrt{\frac{M_A}{M_B}}$$

"The speed of gaseous particles is inversely proportional to the square root of the molar mass at constant Temperature, T". Hence, the higher the molar mass, the lower the average speed of that molecule at constant temperature, T.

Now we can also compare the average speed for particles of a given gas at two different temperatures, T_1 and T_2.

$$v \propto \sqrt{T} \Rightarrow \frac{v_1}{v_2} = \sqrt{\frac{T_1}{T_2}}$$

"The average speed of same gas molecules is directly proportional to the square root of the absolute temperature."

Example 1: Calculate the average speed of O_2 molecules at 25.00 ^oC.

$$v = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.31\ kg.m^2.s^{-2}.mol^{-1}.K^{-1} \times 298.15\ K}{32 \times 10^{-3}\ \frac{kg}{mol}}}$$

$$v_{O_2} = 482\ m/s$$

Example 2: Consider the following gases: He, Cl_2, CH_4, and NH_3. Rank the average speeds of this gases at the same temperature T.

$$\left.\begin{array}{l} He = 4.0 \text{ g/mol} \\ Cl_2 = 71.0 \text{ g/mol} \\ CH_4 = 16.0 \text{ g/mol} \\ NH_3 = 17.0 \text{ g/mol} \end{array}\right\} \quad v_{He} > v_{CH_4} > v_{NH_3} > v_{Cl_2}$$

$$v = \frac{1}{\sqrt{M}}$$

The lower the molar mass, the higher the average speed.
Hence, Helium has the lowest molar mass and the highest average speed.

In Section 5.25, practice the Interactive Problems.

Sections 5.26 - 5.27: Graham's Law of Effusion

Effusion is the flow of gas particles through tiny pores or pinholes. The relative rates of effusion of different gases depend upon the pressure (P) of the gases and the relative speed (v) of gas particles

Consider two gases A and B whose rates of effusion at constant pressure are v_A and v_B, respectively.

Hence, the ratio can be expressed as $\dfrac{\text{rate of effusion B}}{\text{rate of effusion A}} = \dfrac{v_B}{v_A}$

The expression for average speed (v) at constant Temperature (T) is:

$$\frac{v_B}{v_A} = \sqrt{\frac{M_A}{M_B}}$$

Hence, the ratio can be expressed as $\dfrac{\text{rate of effusion B}}{\text{rate of effusion A}} = \sqrt{\dfrac{M_A}{M_B}}$ at constant P and T

This expression is called the **Graham's Law of Effusion** and was discovered in 1829.

"The rate of effusion of a gas is inversely proportional to its molar mass at constant Pressure (P) and Temperature (T)."

Hence, by comparing the rates of effusion of gases at constant Pressure and Temperature, the molar mass of the gas can be determined. The question now is how to determine the rate of effusion.

$$\text{rate} = \frac{\text{distance}}{\text{time}}$$

$$\text{Hence, rate of effusion A} = \frac{\text{distance}}{\text{time}_A} \quad \text{and, rate of effusion B} = \frac{\text{distance}}{\text{time}_B}$$

$$\text{Thus,} \quad \frac{\dfrac{\text{distance}}{\text{time}_B}}{\dfrac{\text{distance}}{\text{time}_A}} = \sqrt{\frac{M_A}{M_B}} \text{ at constant P and T}$$

$$\text{Thus,} \quad \frac{\text{time}_A}{\text{time}_B} = \sqrt{\frac{M_A}{M_B}} \text{ at constant P and T}$$

From this equation, we can conclude that the larger the molar mass, the longer it takes to effuse at constant Pressure and Temperature.

Example: Calculate the ratio of effusion rates of CO_2 and Cl_2 from the same container at constant pressure and temperature.

Use this relationship to calculate the ratio:

$$\frac{\text{rate of effusion B}}{\text{rate of effusion A}} = \sqrt{\frac{M_A}{M_B}} \text{ at constant P and T}$$

$$\frac{\text{rate of effusion } CO_2}{\text{rate of effusion } Cl_2} = \sqrt{\frac{M_{Cl_2}}{M_{CO_2}}}$$

M_{Cl_2} = 71.0 g/mol and M_{CO_2} = 44.0 g/mol

$$\frac{\text{rate of effusion } CO_2}{\text{rate of effusion } Cl_2} = \sqrt{\frac{71.0 \text{ g/mol}}{44.0 \text{ g/mol}}} = 1.27$$

In Section 5.27, practice the Interactive Problem.

Sections 5.28 - 5.29: Real Gases

The equation PV = nRT represents the behavior of gases fairly well under "ordinary conditions" (that is under low pressure and moderate temperature, but not too low).

At sufficiently high pressures and/or sufficiently low temperatures, gases do not behave ideally. Under these conditions PV = nRT does not work well (the volume V taken up by n moles of gas at temperature T and pressure P differs from nRT/P).

At sufficiently high pressures and/or sufficiently low temperatures, it is possible to liquefy a gas.

At sufficiently high pressures and/or sufficiently low temperatures, two of the postulates of the Kinetic Theory of gases are no longer true.

Volume (V) occupied by molecules/atoms is no longer negligible compared to the volume of container.

Attraction between molecules/atoms can no longer be neglected.

Van der Waals modified the ideal gas equation to make it more reliable when the molar volume is small (V_m = V/n is small when T is low or P is large, since V_m = RT/P).

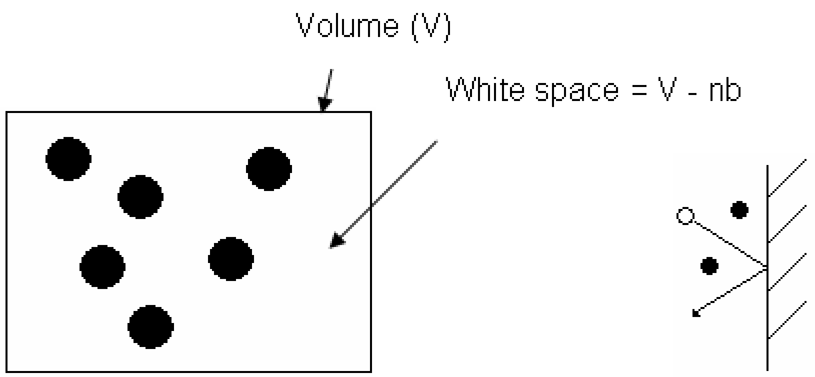
According to Van der Waals P is written as:

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

"**b**" is the excluded molar volume. It accounts for the fact that the volume available for the motion of particles is actually less than the container volume (by an amount equal to nb). b is approximately the volume occupied by a mole of particles.

"**a**" is called the strength of intermolecular interactions. It accounts for the attractions between particles and the fact the collisions of particles with the walls are weaker when particles are attracted by other particles on their way to the wall.

The quantities “a” and “b” in the van der Waals equation depend on the nature of the molecule or the atom. The larger the molecule or the atom, the larger “a” and “b”.



Example: If O_2 were an ideal gas, the pressure of 0 deg.C exerted by 1.000 mol occupying 22.41 L would be 1.000 atm. Use the van der Waals equation to calculate the pressure if a = 1.382 $L^2.atm.mol^{-2}$ and b = 0.03186 $L.mol^{-1}$ Rearrange this equation to calculate for P.

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

n = 1.000 mol
R = 0.0821 $L.atm.mol^{-1}.K^{-1}$
T = 273.15 K
V = 22.41 L

$$P = \frac{1.000\ mol \times 0.0821\ L.atm.mol^{-1}.K^{-1} \times 273.15\ K}{22.41\ L - (1.000\ mol \times 0.03186\ L.mol^{-1})} - \frac{(1.000\ mol^2 \times 1.382\ L^2.atm.mol^{-2})}{(22.41\ L)^2}$$

P = 1.002 atm – 0.0028 atm

P = 0.999 atm

In Section 5.29, practice the Interactive Problem.