GAS LAWS

PROPERTIES OF GASES

- Gases are highly compressible
- Gas particles are further apart relative to liquids or solids
- The volume occupied by gases is mostly empty space
- Gases expand to fill every available space
- Gases are in rapid random motion
- All gases diffuse in one another
- The attraction between gas particles is weaker relative to liquids or solids
- If a fixed sample of gas is left undisturbed at constant V & T, the P of the gas remains constant.

PRESSURE

- **A physical property of matter that describes the force particles have on a surface. Pressure is the force per unit area, P = F/A**
- Pressure can be measured in:
- atmosphere (atm)
- millimeters of mercury (mmHg)
- (torr) after Torricelli, the inventor of the mercury barometer (1643)
- pounds per square inch (psi)

1 atm = 760 mmHg = 760 torr = 14.69 psi = 101.3 kPa

TEMPERATURE

- **A physical property of matter that determines the direction of heat flow.**
- Measured on three scales.
- Fahrenheit °F Celsius °C
- Kelvin K
- **°F = (1.8 °C) + 32 °C = (°F - 32)/1.8**
- **K = °C + 273.15**

At STP, gas molecules are so far apart that for 1 mole of gas, the overall volume does not change.

STP : P = 1 atm & T = 273 K

GAS	WEIGHT	MOLAR VOLUME
H_2	2.0 g/mol	22.4 L/mol
N_2	28.0 g/mol	22.4 L/mol
Xe	131.3 g/mol	22.4 L/mol

AVOGADRO'S HYPOTHESIS

- Avogadro pictured the moving molecule as occupying a small portion of the larger space apparently occupied by the gas. Thus the "volume" of the gas is related to the spacing between particles and not to the particle size itself.
- Imagine 3 balloons each filled with a different gas (He, Ar, & Xe). These gases are listed in increasing particle size, with Xe being the largest atom. According to Avogadro's Hypothesis, the balloon filled with one mole of He will occupy that same volume as a balloon filled with one mole of Xe.
- So for a gas, the "volume" and the moles are directly related. $V \alpha n$

THE PROPERTIES OF GASES

Avogadro's Law
Equal volumes of gas at the same temperature and pressure contain equal numbers of molecules.

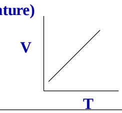
$V \propto n$

$V/n = k$

Charles' Law
The volume of a fixed amount of gas at constant pressure is proportional to the absolute temperature of the gas (absolute – Kelvin temperature)

$V \propto T$ (K)

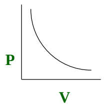
$V/T = k$



Boyle's Law
The volume of a fixed amount of gas at constant temperature is inversely proportional to the gas pressure.

$P \propto 1/V$

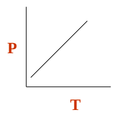
$PV = k$



Gay-Lussac's Law
The pressure of a fixed amount of gas at constant volume is proportional to the absolute temperature of the gas.

$P \propto T$ (K)

$P/T = k$



EMPIRICAL GAS LAWS

Boyle's Law	$P_1V_1 = P_2V_2$
Charles' Law	$V_1 / T_1 = V_2 / T_2$
Guy-Lussac's Law	$P_1 / T_1 = P_2 / T_2$
Avogadro's Law	$V_1 / n_1 = V_2 / n_2$
Combined Gas Law	$P_1V_1 / T_1 = P_2 V_2 / T_2$

Ideal Gas Law PV = nRT

P = pressure (atm) V = volume (L)

n = chemical amount (mol) T = Temperature (K)

R = ideal gas constant = 0.08206 L-atm / mol-K

STOICHIOMETRY & THE GAS LAWS

1. Write a balanced chemical equation
2. Convert to moles (if gas, use PV=nRT or Molar Volume)
3. Use the mole ratio to convert from moles of "A" to moles of "B".
4. Convert moles of "B" to desired measurement, if a gas use PV=nRT.

EXAMPLE:

What volume of gaseous H_2O is produced in the combustion of 348.0 L of C_3H_8?

Combined Gas law vs Stoichiometry

1. A sample of carbon dioxide occupies 0.300 L at 10 °C and 750 torr. What volume will the gas have at 30 °C and 750 torr?

2. We burn methane as a source of energy to heat and cook. What volume of oxygen, measured at 25 °C and 760 torr, is required to react with 1.0 L of methane measured at 45 °C and 625 mmHg?

$$\frac{P_oV_o}{T_o} = \frac{P_fV_f}{T_f}$$

LECTURE QUESTIONS GAS (1)

1. A sample of He gas has a volume of 367.9 mL at a pressure of 0.893 atm. Determine the volume of the gas at STP.

2. How many moles of helium gas are required to fill a 80.05 L balloon with a pressure of 1.546 atm and a temperature of 58.9 °C?

3. A tank of propane provides 7658 L of gas, C_3H_8, at STP. How many tanks of oxygen, each providing 5600. L of oxygen at STP, will be required to burn the propane?

Workshop on Gas Laws (1)

1. A reaction is performed in a vessel attached to a closed-tube manometer. Before the reaction, the levels of mercury in the two sides of the manometer were at the same height. As the reaction proceeds, a gas is produced. At the end of the reaction, the height of the mercury column on the vacuum side of the manometer has risen 35.96 cm and the height on the side of the manometer connected to the flask has fallen by the same amount. What is the pressure in the apparatus at the end of the reaction expressed in (A) torr; (B) Pa; and (C) atm?

2. A sample of gas has a volume of 2.40 mL at a pressure of 0.993 atm. Determine the volume of the gas at a pressure of 0.500 atm.

3. A sample of ammonia occupies 2.670 L at 70 °C and 650 torr. What volume will the gas have at 20 °C and 790 torr?

4. We burn methane as a source of energy to heat and cook. What volume of oxygen, measured at 35 °C and 770 torr, is required to react with 5.0 L of methane measured under the same conditions of temperature and pressure?

5. An acetylene tank for an oxyacetylene welding torch provides 9340 L of acetylene gas, C_2H_2, at STP. How many tanks of oxygen, each providing 7.00×10^3 L of oxygen at STP, will be required to burn the acetylene?

Workshop on Gas Laws (1) ANSWERS

1. A reaction is performed in a vessel attached to a closed-tube manometer. Before the reaction, the levels of mercury in the two sides of the manometer were at the same height. As the reaction proceeds, a gas is produced. At the end of the reaction, the height of the mercury column on the vacuum side of the manometer has risen 35.96 cm and the height on the side of the manometer connected to the flask has fallen by the same amount. What is the pressure in the apparatus at the end of the reaction expressed in (A) torr; (B) Pa; and (C) atm?

2. A sample of gas has a volume of 2.40 mL at a pressure of 0.993 atm. Determine the volume of the gas at a pressure of 0.500 atm. 4.77 mL

3. A sample of ammonia occupies 2.670 L at 70 °C and 650 torr. What volume will the gas have at 20 °C and 790 torr? 1.88 L

4. We burn methane as a source of energy to heat and cook. What volume of oxygen, measured at 35 °C and 770 torr, is required to react with 5.0 L of methane measured under the same conditions of temperature and pressure? 10 L

5. An acetylene tank for an oxyacetylene welding torch provides 9340 L of acetylene gas, C_2H_2, at STP. How many tanks of oxygen, each providing 7.00×10^3 L of oxygen at STP, will be required to burn the acetylene? 3.34 TANKS OF O_2

DALTON'S LAW OF PARTIAL PRESSURES

The total pressure of a mixture of gases equals the partial pressures of each of the constituent gases. Furthermore, a mixture of gases that do not react with one another behaves like a single pure gas.

$$P_{total} = P_{gas\ A} + P_{gas\ B} + P_{gas\ C} \cdots$$

EXAMPLE:
A 250.0 mL sample of a gas mixture was analyzed and found to contain 2.00 g of NO_2 and 1.75 g of SO_3 at 55.0°C. What is the total pressure of the mixture and the partial pressure of each component?

DALTON'S LAW OF PARTIAL PRESSURE & STOICHIOMETRY

EXAMPLE:

In an experiment similar to lab #6 at LACC, 0.2898 g of aluminum metal is dissolved in 35 mL of 3.0 M sulfuric acid. The product gas was collected over water. What volume of gas was produced if the barometer in the room read 752.83 mmHg and 19.8 °C?

Mole Fraction

The easiest way to express the relation between the total pressure of a mixture and the partial pressures of its components is to introduce the mole fraction, χ_J, of each component. The mole fraction is a dimensionless number that expresses the ratio of the number of moles of one component (A) to the total number of moles in the mixture. That is,

$$\chi_A = n_A/(n_A + n_B + \ldots)$$

The partial pressure of a gas is then related to the total pressure by the mole fraction as follows:

$$P_A = \chi_A P_{Total}.$$

This is known as vapor pressure lowering.

DENSITY OF A GAS

The density of a gas at STP can be calculated by

$$d_{STP} = \text{molar mass/molar volume}$$

The density of a gas not at STP can be calculated by

$$d = (MM)\ P\ /\ R\ T$$

Example:
Calculate the density of ozone gas at 30.0 °C and 725 torr.

Workshop on Gas laws (2a)

1. Determine the volume of 655 g methane at 25 °C and 745 torr.

2. How many moles of hydrogen gas are required to fill a 16.80 L balloon with a pressure of 1.050 atm and a temperature of 38 °C?

3. A sample of ammonia is found to occupy 0.250 L under laboratory conditions at 27.0 °C and 0.850 atm. Find the volume under STP conditions.

4. What is the density of ethane gas at a pressure of 183.4 kPa and a temperature of 25.0 °C?

5. Calculate the density of fluorine gas at 30.0 °C and 725 torr.

6 A syringe containing 50.0 mL of vacuum weighs 75.212 g. The same syringe containing 50.0 mL of gaseous butane at a pressure of 0.923 atm and a temperature of 24 °C weighs 75.322 g. What is the molar mass of butane?

7. What volume of oxygen gas at 27.0 °C and 0.899 atm is consumed in the combustion of 702 g of octane?

8. What is the pressure (in kPa) in a 35.0 L balloon at 25.0 °C filled with pure hydrogen gas produced by the reaction of 34.11 g of CaH_2 with water?

Workshop on Gas laws (2a answers)

1. Determine the volume of 655 g methane at 25 °C and 745 torr. 1.0 x 10^3 L

2. How many moles of hydrogen gas are required to fill a 16.80 L balloon with a pressure of 1.050 atm and a temperature of 38 °C? 0.69 mol

3. A sample of ammonia is found to occupy 0.250 L under laboratory conditions at 27.0 °C and 0.850 atm. Find the volume under STP conditions. 0.193 L

4. What is the density of ethane gas at a pressure of 183.4 kPa and a temperature of 25.0 °C? 2.22 g/L

5. Calculate the density of fluorine gas at 30.0 °C and 725 torr. 1.46 g/L

6 A syringe containing 50.0 mL of vacuum weighs 75.212 g. The same syringe containing 50.0 mL of gaseous butane at a pressure of 0.923 atm and a temperature of 24 °C weighs 75.322 g. What is the molar mass of butane? 58.0 g/mol

7. What volume of oxygen gas at 27.0 °C and 0.899 atm is consumed in the combustion of 702 g of octane? 2106 L

8. What is the pressure (in kPa) in a 35.0 L balloon at 25.0 °C filled with pure hydrogen gas produced by the reaction of 34.11 g of CaH_2 with water? 115 kPa

Workshop on Gas Laws (2b)

9. Sulfur dioxide is an intermediate in the preparation of sulfuric acid. What volume of SO_2 at 343 °C and 1.21 atm is produced by burning 1.00 kg of sulfur in oxygen?

10. What is the total pressure (in atm) in a 10.0 L vessel that contains 2.50 x 10^{-3} mol of H_2, 1.00 x 10^{-3} mol of He, and 3.00 x 10^{-4} mol of Ne at 35°C?

11. If 0.200 L of argon is collected over water at a temperature of 26 °C and a pressure of 750 torr, what is the partial pressure of argon? *Note: the vapor pressure of water at 26 °C is 25.2 torr.*

12. A mixture of oxygen and helium contains 92.3% by mass O_2. What is the partial pressure of oxygen being administered if atmospheric pressure is 730 torr?

13. A neon-oxygen gas mixture contain 141.2 g of oxygen and 335.0 g of neon. The pressure in this gas tank is 50.0 atm. What is the partial pressure of oxygen in the tanks?

14. Ammonium nitrite decomposes upon heating to form nitrogen gas and water. When a sample is decomposed in a test tube, 511 mL of nitrogen gas is collected over water at 26 °C and 745 torr total pressure. How many grams of ammonium nitrite were decomposed? *Note: the vapor pressure of water at 26 °C is 25.2 torr.*

Kinetic Molecular Theory

- Matter is composed of tiny particles (atoms, molecules or ions) with definite and characteristic sizes that never change.
- The particles are in constant random motion, that is they possess kinetic energy. $E_k = {}^1/_2\ mv^2$
- The particles interact with each other through attractive and repulsive forces (electrostatic interactions), that is the possess potential energy. U = mgh
- The velocity of the particles increases as the temperature is increased therefore the average kinetic energy of all the particles in a system depends on the temperature.
- The particles in a system transfer energy form one to another during collisions yet no net energy is lost from the system. The energy of the system is conserved but the energy of the individual particles is continually changing.

Kinetic Molecular Theory of Gases – an explanation of the properties of an ideal gas in terms of the behavior of continuously moving molecules that are so small that they can be regarded as having no volume. This theory can be summed up with the following five postulates about the molecules of an ideal gas:

1. Gases are composed of molecules that are in continuous motion. The molecules of an ideal gas move in straight lines and change direction only when they collide with other molecules or with the walls of the container.

2. The molecules of a gas are small compared to the distances between them; molecules of an ideal gas are considered to have no volume. Thus, the average distance between the molecules of a gas is large compared to the size of the molecules.

3. The pressure of a gas in a container results from the bombardment of the walls of the container by the molecules of the gas.

4. Molecules of an ideal gas are assumed to exert no forces other than collision forces on each other. Thus the collisions among molecules and between molecules and walls must be elastic; that is, the collisions involve no loss of energy due to friction.

5. The average kinetic energy of the molecules is proportional to the Kelvin temperature of the gas and is the same for all gases at the same temperature.

Furthermore, the speed (or velocity) of these molecules can be related to temperature via the following, known as the root mean square speed (u_{rms})

$$u_{rms} = \sqrt{\frac{3RT}{M}}$$

where R = 8.3145 J/K mol; T = temperature in Kelvin, and M = molar mass in kg/mol. The model of the kinetic molecular theory of gases is consistent with the ideal gas law and provides the aforementioned expression for the root mean square speed of molecules. When combining root mean square speed with the expression for kinetic energy (which we know is ½ mv^2 PER MOLECULE), one can derive an equation for the kinetic energy of an ideal gas PER MOLE:

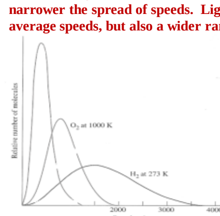
$$\text{KE (per mole)} = \tfrac{1}{2} mv^2 = \tfrac{1}{2} m \left(\sqrt{\frac{3RT}{M}}\right)^2 = 3/2\ RT$$

Once again, we see that molar kinetic energy of a gas is proportional to the temperature.

Maxwell Distribution of Speeds – As useful as the root mean square equation is for most gases, it only represents an *average* speed. Individual molecules undergo several billion changes of speed and direction each second. The formula for calculating the fraction of gas molecules having a given speed at any instant was first derived by James Maxwell. You should be familiar with the conceptual implications of this equation:

1. The molecules of all gases have a wide range of speeds. As the temperature increases, the root mean square speed and the range of speeds both increase. The range of speeds is described by the Maxwell distribution (equation).

2. Heavy molecules (such as CO_2) travel with speeds close to their average values. The greater the molar mass, the lower the average speed and the narrower the spread of speeds. Light molecules (such as H_2) not only have higher average speeds, but also a wider range of speeds.



For example, some molecules of gases with low molar masses have such high speeds that they can escape from the gravitational pull of small planets and go off into space. As a consequence, hydrogen molecules and helium atoms, which are both very light, are rare in the Earth's atmosphere.

PROPERTIES OF GASES

- DIFFUSION

Diffusion is the ability of two or more gases to mix spontaneously until a uniform mixture is formed.

Example: A person wearing a lot of perfume walks into an enclosed room, eventually in time, the entire room will smell like the perfume.

- EFFUSION

Effusion is the ability of gas particles to pass through a small opening or membrane from a container of higher pressure to a container of lower pressure.

The General Rule is: The lighter the gas, the faster it moves.

Graham's Law of Effusion:

$$\frac{\text{Rate of effusion of gas A}}{\text{Rate of effusion of gas B}} = \sqrt{(\text{molar mass B / molar mass A})}$$

The rate of effusion of a gas is inversely proportional to the square root of the molar mass of that gas.

Workshop (3) on Effusion

1. Calculate the ratio of the rate of effusion of hydrogen to the rate of effusion of oxygen.

2. A gas of unknown identity effuses at the rate of 169 mL s^{-1} in a certain effusion apparatus in which carbon dioxide effuses at the rate of 102 mL s^{-1}. Calculate the molar mass of the unknown gas.

3. An unknown gas composed of homonuclear diatomic molecules effuses at a rate that is only 0.355 times that of O_2 at the same temperature. What is the identity of the unknown gas?

4. It took 4.5 min for helium to effuse through a porous barrier. How long will it take the same volume of Cl_2 gas to effuse under identical conditions?

Real Gases: Deviations from Ideality

To review, molecules of an ideal gas have no significant volume and do not attract each other. Real gases approximate this behavior at low pressures and elevated temperatures; real gases deviate from ideality at *high pressures* and *low temperatures*.

The molecules in a real gas at relatively low pressure have practically no attraction for one another, because they are far apart. Thus they behave almost like molecules of ideal gases. However, if they crowd the molecules close together by increasing the pressure, then the effect on the force of attraction between the molecules increases (*see "P" correction for molecular attraction on the next slide*).

Real Gases: Deviations from Ideality

In the case of low temperatures, intermolecular attraction between molecules is more pronounced because the molecules move more slowly, their kinetic energy is smaller relative to the attractive forces, and they fly apart less easily after collisions with one another. This results in a decrease in *volume (see "V" correction for volume of molecules below)*.

An equation by Johannes van der Waals was constructed in 1879 to correct for the volume of real gas molecules and the attractive forces that exist between them:

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

("P" correction) ("V" correction)

Real Gases: Deviations from Ideality

The variables, *a* and *b* are constants that depend on the gas (this information will be provided on a case-by-case basis) known as the van der Waals parameters, and the other terms have their usual meaning in a gas equation. The parameter *a* represents the role of attractive forces, and *b* represents the role of repulsive forces. Once these parameters have been determined, they can be used in the van der Waals equation to predict the pressure of a certain gas under the conditions of interest.

The van der Waals parameters will be given on a case-by-case basis, depending on the identity of your particular gas. Note that the values of BOTH *a* and *b* generally INCREASE with an increase in mass of the molecule and with an increase in the complexity of its structure. Larger, more massive molecules not only have larger volumes, they also tend to have greater intermolecular attractive forces.

Lecture Problems on Effusion & Molecular speed

1. A sample of oxygen was found to have to effuse at a rate equal to 2.83 times that of an unknown homonuclear diatomic gas. What is the molar mass of the unknown gas. Identify the gas.

2. Place the following gases in order of increasing average molecular speed at 25.0 °C.

CO, SF_6, H_2S, Cl_2, HI

3. Calculate the rms speed of CO and SF_6 at 25.0 °C.

Workshop (4) on KMT & Real Gases

1. Estimate the root mean square speed of water molecules in the vapor above boiling water at 100 °C.

2. Calculate the average kinetic energy (in J) of a sample of 1 mole Ne(g) at 25.00 °C.

3. Calculate the pressure at 298 K exerted by 1.00 mol of hydrogen gas when confined in a volume of 30.0 L. Repeat this calculation using the van der Waals equation. What does this calculation indicate about the accuracy of the ideal gas law?

***Note*: For H_2, a = 0.2476 atm L^2/mol^2 and b = 0.02661 L/mol**