Chapter 5: Gases

**Homework:** Read Chapter 5. Work out sample/practice exercises

*Keep up with MasteringChemistry assignments*

**Gas Properties:**

Gases have high kinetic energy, low density (measured in g/L), homogeneous mixing, gases take on the volume and shape of its container, gases exert pressure, gases are compressible and expandable.

**Ideal Gas:**

An ideal gas consists of tiny particles in constant, random, straight-line motion. The volume of the particles themselves is negligible compared to the total volume of the gas, there is a lot of empty space. Particles ideally exhibit no attraction or repulsion between each other. Collisions of gas particles are ideally elastic. The total kinetic energy is constant at constant T. The average kinetic energy of gas particles is proportional to the Temperature in Kelvin.

**Gas Pressure:**

Gas pressure is the result of collisions by gas molecules with surfaces around them. Factors affecting pressure: number of particles, volume, average speed.

Pressure can be measured by barometers or manometers.

**Barometer**

Pressure is Force per unit Area...

\[
P = \frac{\text{Force}}{\text{Area}} = \frac{\text{mass} \times \text{acceleration}}{\text{Area}}
\]
The SI unit for pressure is Pascal is very small.

\[ 1 \text{ Pa} = \frac{\text{kg m}}{\text{s}^2} = \frac{\text{kg/m}^2}{\text{s}^2} = \text{kg/m}^2, \text{ where N is a Newton (kg m/s}^2) \]

Pressure on a mountaintop is less than sea level and those are less than low places like Death Valley. Variations in atmospheric pressure creates wind and weather.

*We will more commonly use units of atmospheres or torr (mm Hg). Evangelista Torricelli (1608-1647) measured pressure with a mercury barometer.*

- 1 atm = 760 torr or 760 mm Hg (if water it would be 10.3 m high)
- 1 atm = 29.92 inches of Hg
- 1 atm = 10132.5 Pa (1Pa = 1 N/m^2) or 101325 kPa or 1.01325 bar
- 1 atm = 14.7 psi

**Example 1:** Convert 748 torr to the following units…

a) atm, b) Pa, c) bar, d) psi

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**The Gas Laws:** All the gas laws apply to all pure gases, regardless of chemical identity or mixtures.

- **Boyle’s Law (1662):** \( PV = k \) or \( P_1V_1 = P_2V_2 \)
- **Charles’s Law (1787):** \( V/T = \text{constant or } V_1/T_1 = V_2/T_2 \) (must use Kelvin!)
- **Gay-Lussac’s Law of Combining Volumes (1808):** At constant temperature and pressure, the volumes of gases involved in chemical reactions are in ratios of small whole numbers. 1 volume of \( N_2 \) + 3 volume of \( H_2 \) = 2 volumes of \( NH_3 \) (all gases)
- **Avogadro’s Law (1810):** \( V/n = \text{constant or } V_1/n_1 = V_2/n_2 \)
- **Ideal Gas Law (first stated by Clapeyron in 1834):** \( PV = nRT, \) where \( R = 0.08206 \text{ L atm/mol K} \)
- **Combined Gas Law:** \[ \frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2} \]
Variations of Ideal Gas Law:

\[ \text{MW} = \frac{\text{mass}\cdot R \cdot T}{P \cdot V} \]

\[ \text{Density} = \frac{(\text{MW})\cdot P}{R \cdot T} \]

**Standard Conditions, STP:**

Standard Temperature and Pressure is at 0°C or 273.15K and 1 atm or 760 torr

Molar volume under STP conditions for an ideal gas = 22.4 L/mol

*Note: Some scientists redefined STP as 1 bar in place of 1 atm. By this new definition the standard molar volume is 22.7 L/mol. We will use the original standard for this class.*

**Dalton’s Law of Partial Pressure (1801):**

\[ P_{\text{total}} = P_1 + P_2 + P_3 \ldots \] at constant V and T (same container)

This law of partial pressures is especially important when collecting gas by displacement of water. One must subtract the partial pressure due to the vapor pressure of water in the closed container. Vapor pressure is dependent on temperature and can be found in reference sources.

**Mole Fraction of A:**

\[ X_A = \frac{\text{moles of } A}{\text{total moles}} = \frac{\text{partial pressure of } A}{\text{total pressure}} \]

**Collecting Gases over Water:**

All closed containers partially filled with liquid have some particles of that liquid in the gas state above the liquid level. Any gas collected by water displacement will be contaminated with water vapor. This amount depends on the temperature.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Pressure (mmHg)</th>
<th>Temperature °C</th>
<th>Pressure (mmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<td>31.9</td>
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<tr>
<td>5</td>
<td>6.54</td>
<td>40</td>
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<td>10</td>
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<td>50</td>
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<td>75</td>
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<td>20</td>
<td>17.55</td>
<td>100</td>
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<tr>
<td>25</td>
<td>23.78</td>
<td>110</td>
<td>1075</td>
</tr>
</tbody>
</table>

*Note: The vapor pressure of water at its normal boiling point is equivalent to 1 atm.
Gas Stoichiometry:

Stoichiometry (mole to mole relationships from a balanced reaction) can be performed starting or ending with gases.

Convert the known amounts to moles, work the mole to mole relationship, convert to what is requested.

**Special case:** When all volumes are measured at the same temperature and partial pressures the mole to mole ratio is equivalent to a volume to volume ratio in a balanced chemical reaction. *Gay-Lussac’s Law of Combining Volumes (1808)*

**Practice with gas problems.**

*Example 2:*

Balance the equation and calculate the liters of CO₂ gas produced for every 9.00 liters of O₂ gas consumed in the combustion reaction below. Both CO₂ and O₂ gases are measured at STP conditions.

\[ \text{C}_4\text{H}_{10} \text{(l)} + \text{O}_2 \text{(g)} \rightarrow \text{CO}_2 \text{(g)} + \text{H}_2\text{O} \text{(l)} \]

*Example 3:*

The most important uses of ammonium nitrate (NH₄NO₃) are in fertilizer and explosives. When ammonium nitrate is heated to 800°C, it decomposes explosively into nitrogen gas (N₂), oxygen gas (O₂), and water vapor (H₂O).

\[ 2 \text{NH}_4\text{NO}_3 \text{(s)} \rightarrow 4 \text{H}_2\text{O} \text{(g)} + \text{O}_2 \text{(g)} + 2 \text{N}_2 \text{(g)} \]

What total number of **moles** and **volume** of the combined gas products measured at 800°C and 745 torr, will formed from 100 pounds of ammonium nitrate reactant?
Example 4:

Hydrogen gas is produced by the reaction of sodium metal with an excess of hydrochloric acid solution. The hydrogen gas was collected by water displacement at 22°C in a 127 ml container with a total pressure of 748 torr. The vapor pressure of water at 22°C is 19.8 torr.

a) What mass of sodium metal was consumed in the reaction?

b) What is the volume of dry H₂ gas at STP?

Example 5:

A foul smelling gas produced by the reaction of HCl with Na₂S was collected. A 2.00 L sample of the product gas had a mass of 3.04 grams at STP. Solve for the molecular weight of the gas and determine its likely identity.
Example 6:
A 4.50 liter helium balloon is given to a small child by the sea. It is a nice warm day of 30°C and 1 atm. pressure. Unhappily, the child lets go of the balloon and it rises up into the air. At a new higher altitude the pressure is 703 torr and Temperature is 10°C. What is the new volume of the balloon?

Example 7:
The density of a gas at STP is 0.7143 g/L. Is this gas CH₄, Ar, CO₂, or Cl₂?
Example 8:

Typically, when a person coughs, he or she first inhales about 2.0-L of air at 1.0-atm pressure and 25°C. The epiglottis and the vocal cords then shut, trapping the air in the lungs, where it is warmed to 37°C and compressed to 1.7-L by action of the diaphragm and chest muscles. The sudden opening of the epiglottis and vocal cords releases this air explosively. What is the approximate pressure of the gas inside the lungs just before the cough?

Example 9:

A heliox deep-sea diving mixture contains 12.0 g of oxygen to every 88.0 g of helium. Solve for the partial pressure of O₂ gas when this mixture is delivered at 100 meters depth with a total pressure of 11.0 atm. (at the surface it is about 1 atm and each 10 m depth under water adds 1 atm pressure)
Example 10:
Hydrogen gas, formed from the chemical reaction of solid zinc and excess hydrochloric acid, is collected over water. The total pressure of the collected gas at 25°C is 747 torr and occupies 843 ml.

a) Write out the balanced reaction and classify the type of reaction.
b) Solve for the partial pressure of the hydrogen gas alone.
c) Solve for the moles of Hydrogen gas collected
d) Solve for the grams of zinc that must react to form the hydrogen gas.

Kinetic Molecular Theory (KMT) of Gases:
Assumptions for the KMT…
1) An ideal gas consists of tiny particles in constant, random, straight-line motion.
2) The volume of the particles themselves is negligible compared to the total volume of the gas.
3) Particles exhibit no attraction or repulsion between each other.
4) Collisions of gas particles are elastic.
5) The average kinetic energy of gas particles is proportional to the Temperature in Kelvin.

These assumptions assist in explaining the properties and behavior of gases and lead to the gas equations. Properties of gases: expand to fill container, take shape of container, low density, compressible, mixtures are homogeneous.
Gas Equations that can be concluded through the Kinetic Molecular theory…

The derivations are to show you where these equations come from, but derivations are not on a test. You should know the end results, formulas…

1) \( PV = nRT \) \( \quad ( R = 0.08206 \text{ L atm/mol K}) \)
2) \( E_k = \frac{3}{2}RT \) \( \quad ( R = 8.314 \text{ J/mol K}) \)
3) \( u_{rms} = \sqrt{\frac{3RT}{MW}} \) \( \quad ( R = 8.314 \text{ kg m}^2/\text{s}^2\text{mol K}, \text{ and } MW \text{ is kg/mol}) \)
4) \( \frac{\text{Rate}_1}{\text{Rate}_2} = \sqrt{\frac{MW_2}{MW_1}} = \frac{\text{speed}_1}{\text{speed}_2} = \frac{\text{distance}_1}{\text{distance}_2} = \frac{\text{time}_2}{\text{time}_1} \)

Recall that…

\( J = \text{kg m}^2/\text{s}^2 \)
\( L = 1 \text{ dm}^3 = \text{m}^3/1000 \)
\( 1 \text{ Pa} = \text{N/m}^2 = \text{kg/m s}^2 = \text{J/m}^3 \)
so that… \( 1 \text{ kPa} = 1 \text{ J/L} \)
and \( 1 \text{ atm} = 101.3 \text{ kPa} = 101.3 \text{ J/L} \)

R constants: set up a dimensional analysis equation from the result above…

\( 0.08206 \text{ L atm/mol K} * 101.3 \text{ J/L atm} = 8.314 \text{ J/mol K} \)

Deriving the Ideal Gas Law: \( PV = nRT \)
P is proportional to the impulse imparted per collision \((mu)\) times the rate of collisions \((n/V \times u)\). \( m = \text{mass}, u = \text{speed}, n = \text{number of particles}, V = \text{volume} \)

\[ P \propto (mu) \times (n/V \times u) \]
which gives us… \( P \propto nmu^2/V \)

Since the average kinetic energy, \( \frac{1}{2}mu^2 \), is directly proportional to \( T \),

\[ mu^2 \propto T \]

Therefore… \( P \propto nT/V \), which leads to…

\[ P = nRT/V, \text{ also known as } PV = nRT \]
Deriving $E_k = \frac{3}{2}RT$ for 1 mole of any ideal gas

Starting with…

\[ P \propto \frac{nmu^2}{V} \]

Pressure on a wall is caused by particles hitting the wall. Some particles will hit perpendicular to the wall giving a full force of pressure while other particles will hit a wall of the container at various angles for 90° (full force to nearly 0° (no force)). Using calculus, the average force of all possible particle hits equals 1/3. This leads to…

\[ P = \frac{1}{3} \frac{nmu^2}{V} \]

rearrange

\[ PV = \frac{1}{3} nmu^2 \]

replace PV with nRT

\[ nRT = \frac{1}{3} nmu^2, \]

$E_k = \frac{1}{2}mu^2$ so…

\[ RT = \frac{1}{3}(2)\left(\frac{1}{2}mu^2\right) \]

which leads to

\[ RT = \frac{2}{3} E_k. \]

Rearrange

\[ E_k = \frac{3}{2}RT \]

$E_k$ is in J/mol  \hspace{1cm} Use $R = 8.314\text{ J/mol K}$

$J/mol K$
Deriving the root mean squared speed, $u_{rms} = \sqrt{\frac{3RT}{MW}}$

We learned that

$$E_k = \frac{3}{2}RT \text{ and } E_k = \frac{1}{2}mu^2$$

therefore

$$\frac{1}{2}mu^2 = \frac{3}{2}RT$$

rearrange

$$u^2 = \frac{3RT}{m}$$

molecular weight = mass of 1 mole

$$u^2 = \frac{3RT}{MW}$$

one more step

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

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**Example 11:**

a) Calculate the average kinetic energy of 1 mole of HF or O$_2$ at 27°C.

b) Which has the smaller root mean squared speed, $u_{rms}$, at 27°C; O$_2$ or HF? Explain.

c) Calculate the $u_{rms}$, at 27°C for the one with slower speed.
Molecular Effusion and Diffusion:

Mean free path is the average distance traveled by a molecule between collisions. Mean free path increases as the pressure decreases.

Effusion is the escape of gas molecules through a tiny hole as helium may leak out of a party balloon and cause the balloon to shrink over time.

Diffusion is the spread of one substance throughout a space. A spill of perfume may diffuse throughout a room.

Graham’s Law of Effusion/Diffusion:

\[
\frac{Rate_1}{Rate_2} = \sqrt{\frac{MW_2}{MW_1}}
\]

Expanding the law …

\[
\frac{Rate_1}{Rate_2} = \sqrt{\frac{MW_2}{MW_1}} = \frac{u_1}{u_2} = \frac{distance_1}{distance_2} = \frac{time_2}{time_1}
\]

Example 12:

a) The velocity of H₂ gas is found to be 4.36 times the velocity of an unknown gas. Calculate the molecular weight of the unknown gas.

b) Given that this gas is one of the diatomic elements, what is the unknown gas?
Example 13:

A sample of neon effuses from a container in 76 seconds. The same number of particles of an unknown noble gas requires 155 seconds. Identify the gas.

Van der Waals Equation for “Real” gases (1873):

Not all gases behave “ideally”.

As temperature decreases the attraction forces between particles start to influence the gas as it prepares for condensation. (a)

As pressures increase the volume taken by the particles is no longer negligible. (b)

Corrections: Constants $a$ and $b$ are found in tables in reference books/sites.

$$a \text{ (attractions} \rightarrow \text{correction for intermolecular forces)}$$
$$b \text{ (bigness or size} \rightarrow \text{correction for particle volume)}$$

$$(P+n^2a/V^2)(V – nb) = nRT$$

<table>
<thead>
<tr>
<th>Gas</th>
<th>$a$ (L$^2$ atm/mol$^2$)</th>
<th>$b$ (L/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0.0342</td>
<td>0.02370</td>
</tr>
<tr>
<td>Kr</td>
<td>2.32</td>
<td>0.0398</td>
</tr>
<tr>
<td>N$_2$</td>
<td>1.39</td>
<td>0.0318</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>6.49</td>
<td>0.0562</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>5.46</td>
<td>0.0305</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>3.59</td>
<td>0.0427</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>20.4</td>
<td>0.1383</td>
</tr>
</tbody>
</table>

Example 14:

Consider a sample of 1.000 mole CO$_2$ gas confined to a volume of 3.000 liters at 0.0°C. Calculate the pressure of the gas using (a) the ideal gas equation and (b) the van der Waals equation. For CO$_2$, $a = 3.59$ L$^2$ atm/mol$^2$ and $b = 0.0427$ L/mol.
Earth’s Atmosphere:

Four regions of the atmosphere are defined based on the temperature variations. Pressure decreases exponentially the higher you go. Look over Figure 5.27 on page 218. Read about air pollution and Ozone depletion.

1. **Thermosphere**: Highest altitude: above 85 km, starting at 180K and warming up a bit as the altitude rises
2. **Mesosphere**: 50-85 km up, starting around 270K and cooling as it increases altitude to about 180K
3. **Stratosphere**: 15-50 km above earth, starting at 220K warming to 270K
4. **Troposphere**: Our level (0-15km) which starts warm (weather) and cools at higher altitudes.
Gas Problems:

1. Two separate containers have the same volume and temperature. The first contains 0.50 moles of CO₂ gas and the second contains 0.75 moles of CH₄ gas. State if the following properties of CO₂ are greater than, less than, or equal to these properties of CH₄.
   a) Pressure of gas in containers CO₂ is _____________ CH₄
   b) Density of gas in containers CO₂ is _____________ CH₄

2. 
   a) What are the characteristics (kinetic molecular theory) of an ideal gas?
   b) How is a real gas different and under what circumstances does a gas become less ideal.
   c) What is the Van der Waals equation?
   d) How are the constants a and b affected by size of molecule and intermolecular attractions?

3. How did the relationship between volume and temperature of a gas at constant pressure and number of moles help determine absolute zero temperature.

4. What is the volume of 32.7 grams of F₂ gas at STP?

5. What is the number of moles of gas in a 550-ml container at 30.0°C and 751 torr pressure?

6. 534-mL of CH₄ gas was collected at 23°C and 754 torr. What new volume would the CH₄ gas occupy at 732 torr and 46°C?

7. 127 ml of N₂ gas was collected by displacement of water at 25°C and 742 torr. What is the number of moles of N₂ gas? (The vapor pressure of water at 25°C is 24 torr.)

8. What pressure will 4.15 g of CO₂ gas have when placed in a 320-mL container at 45.0°C?

9. Nitrogen gas is placed into a steel tank until its pressure is 21.4 atm at 20°C. The maximum pressure the tank can safely contain is 50.0 atm. What is the highest temperature in °C that this tank be safely heated.

10. Solve for the mole fraction of each component in a mixture of 12.0 g H₂, 60.0 g N₂ and 2.50 g of NH₃ gases. Solve for the total pressure and partial pressures of each if the gas mixture is in a 100.0 L container at 22.5°C.
11. a) Balance the following unbalanced equation:
\[ \text{C}_5\text{H}_{12} (g) + \text{O}_2 (g) \rightarrow \text{CO}_2 (g) + \text{H}_2\text{O} (g) \]

b) What volume of CO\(_2\) gas at STP will be produced from 144 g of C\(_5\)H\(_{12}\)?

12. Balance \( \text{H}_2 (g) + \text{N}_2 (g) \rightarrow \text{NH}_3 (g) \) all gases at same temperature and pressure.
How many cubic centimeters of H\(_2\) gas are required to produce 200 cm\(^3\) of ammonia gas?

13. A 2.135-g gas sample occupies 315.5 ml at 739.2 mm Hg and 26.1\(^\circ\)C. Analysis of the compound shows it to be 14.05\% C, 41.48\% Cl, and 44.46\% F by mass. What is the molecular formula?

14. Which of the following occupies the greatest volume when measured at STP?
   a) 30.0 g O\(_2\) b) 1.10 mol SO\(_2\) c) 20.0 L CO d) 7.2 \times 10^{23} molecules Cl\(_2\)

15. Calculate the density of chlorine gas at 80\(^\circ\)C and 3.00 atmospheres pressure.

16. A sample of Ar (g) effuses through a tiny hole in 45.1 seconds. How long would it take for a sample of SF\(_4\) gas to effuse under the same conditions?

17. Carbon dioxide gas (CO\(_2\)) is collected over water in a 544 ml container at 23.0\(^\circ\)C and equalized with the room pressure of 750 torr. The vapor pressure of water at 23.0\(^\circ\)C is 21.1 torr. What volume will this same sample of dry CO\(_2\) gas occupy under STP conditions?