10.1: Characteristics of Gases

Bulk matter can exist in three states: gas, liquid, and solid. Gases have the lowest density of the three, are highly compressible, and fill their containers completely. Elements that exist as gases at room temperature and pressure are clustered on the right side of the periodic table; they occur as either monatomic gases (the noble gases) or diatomic molecules (some halogens, $N_2$, $O_2$).

- Gases expand spontaneously to fill containers in which they are held, equaling their volume. Consequently, they are highly compressible.
- Gases form homogeneous mixtures with each other regardless of the identities or relative proportions of the component gases.
- The characteristic properties of gases arise because the individual molecules are relatively far apart, hence, acting largely as though they were alone.

10.2: Pressure

Pressure is defined as the force exerted per unit area; it can be measured using a barometer or manometer. Four quantities must be known for a complete physical description of a sample of a gas: temperature, volume, amount, and pressure. Pressure is force per unit area of surface; the SI unit for pressure is the pascal (Pa), defined as 1 newton per square meter ($N/m^2$). The pressure exerted by an object is proportional to the force it exerts and inversely proportional to the area.

- Pressure, $P$, is the Force, $F$, that acts on a given Area, $A$:
  \[ P = \frac{F}{A} \]

Atmospheric Pressure and the Barometer

- The force, $F$, exerted by any object is the product of its mass, $m$, times its acceleration, $a$: $F = ma$
- SI unit for force is kg-m/s$^2$ and is called the Newton (N)
- SI unit of pressure is N/m$^2$, called a Pascal
- Standard atmospheric pressure: defined as 760 torr (760 mm Hg), or, in SI units, 101.325 kPa
- Atmosphere: unit of pressure equal to 760 torr; 1 atm = 101.325 kPa

10.3: The Gas Laws

The volume of a gas is inversely proportional to its pressure and directly proportional to its temperature and the amount of gas. Boyle showed that the volume of a sample of a gas is inversely proportional to pressure (Boyle’s law), Charles and Gay-Lussac demonstrated that the volume of a gas is directly proportional to its temperature at constant pressure (Charles’s law), and Avogadro showed that the volume of a gas is directly proportional to the number of moles of gas
The Pressure-Volume Relationship: Boyle’s Law

- Boyle’s law states that the volume of a fixed quantity of gas maintained at constant temperature is inversely proportional to the pressure. When two measurements are inversely proportional, one gets smaller as the other one gets larger.

\[ PV = \text{constant} \]

where \( P \) = pressure, \( V \) = volume

The Temperature-Volume Relationship: Charles’s Law

- Charles’s law: states that the volume of a fixed amount of gas maintained at constant pressure is directly proportional to its absolute temperature. Thus, as the pressure gets higher, so does the temperature.

\[ \frac{V}{T} = \text{constant} \]

where \( V \) = volume, \( T \) = Temperature

The Quantity-Volume Relationship: Avogadro’s Law

- Law of combining volumes: at a given pressure and temperature, the volumes of gases that react with one another are in the ratios of small whole numbers. (ie: \( 2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O} \))
- Avogadro’s hypothesis: equal volumes of gases at the same temperature and pressure contain equal number of molecules
- Avogadro’s law: The volume of a gas maintained at constant temperature and pressure is directly proportional to the number of moles of the gas

\[ V = \text{constant} \times n \]

where \( V \) = volume, \( n \) = number of moles

10.4: The Ideal Gas Equation

The empirical relationships among the volume, the temperature, the pressure, and the amount of a gas can be combined into the ideal gas law, \( PV = nRT \). The proportionality constant, \( R \), is called the gas constant. The ideal gas law describes the behavior of an ideal gas, a hypothetical substance whose behavior can be explained quantitatively by the ideal gas law and the kinetic molecular theory of gases. Standard temperature and pressure (STP) is 0°C and 1 atm.

Ideal-gas equation

\[ PV = nRT \]

where \( P \) = pressure, \( V \) = volume, \( n \) = number of moles, \( R \) = gas constant, \( T \) = Temperature (always expressed on absolute-temperature scale, usually Kelvin)
The **Gas constant** \((R)\) is the constant of proportionality in the ideal-gas equation. Some values of \(R\) are given below:

<table>
<thead>
<tr>
<th>Units</th>
<th>Numerical value</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-atm/mol-K</td>
<td>0.08206</td>
</tr>
<tr>
<td>Cal/mol-K</td>
<td>1.987</td>
</tr>
<tr>
<td>J/mol-K</td>
<td>8.314</td>
</tr>
<tr>
<td>M^3-Pa/mol-K</td>
<td>8.314</td>
</tr>
<tr>
<td>L-torr/mol-K</td>
<td>62.36</td>
</tr>
</tbody>
</table>

**Standard temperature and pressure** (STP): 0°C and 1 atm. 1 mol of gas at STP has a volume of 22.41 L (**molar volume**)

### 10.5: Further Applications of the Ideal-Gas Equations

The relationship between the amounts of products and reactants in a chemical reaction can be expressed in units of moles or masses of pure substances, of volumes of solutions, or of volumes of gaseous substances. The ideal gas law can be used to calculate the volume of gaseous products or reactants as needed. In the laboratory, gases produced in a reaction are often collected by the displacement of water from filled vessels; the amount of gas can be calculated from the volume of water displaced.

Density of a gas \(\rho\) = density, \(M\) = molar mass:

\[
\rho = \frac{PM}{RT}
\]

Molar mass of a gas:

\[
M = \frac{\rho RT}{P}
\]

### 10.6: Gas Mixtures and Partial Pressures

The pressure exerted by each gas in a gas mixture is independent of the pressure exerted by all other gases present. Consequently, the total pressure exerted by a mixture of gases is the sum of the partial pressures of the components (Dalton’s law of partial pressures). The amount of gas in a mixture may be described by its partial pressure or its mole fraction. In a mixture, the partial pressure of each gas is the product of the total pressure and the mole fraction.

- **Partial pressure**: the pressure exerted by a particular gas in a mixture
- **Dalton’s law of partial pressures**: law stating that the total pressure of a mixture of gases equals the sum of the pressures that each would exert if it were present alone

The total pressure at constant temperature and volume is determined by the total number of moles of gas present, whether that total represents just one substance or a mixture.
Partial Pressures and Mole Fractions

- **Mole fraction**: the ratio of the number of one component of a mixture to the total moles of all components; abbreviated \(\chi\), with a subscript to identify the components.

The partial pressure of a gas in a mixture is its mole fraction times the total pressure.

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### 10.7: Kinetic-Molecular Theory

*The behavior of ideal gases is explained by the kinetic molecular theory of gases. Molecular motion, which leads to collisions between molecules and the container walls, explains pressure, and the large intermolecular distances in gases explain their high compressibility. Although all gases have the same average kinetic energy at a given temperature, they do not all possess the same root mean square speed. The actual values of speed and kinetic energy are not the same for all gas particles.*

**Kinetic-molecular theory**: set of assumptions about the nature of gases. These assumptions, when translated into mathematical form, yield the ideal-gas equation:

1. Gases consist of large numbers of molecules that are in continuous, random motion
2. The volume of all the molecules of the gas is negligible compared to the total volume in which the gas is contained
3. Attractive and repulsive forces between gas molecules are negligible
4. Energy can be transferred between molecules during collisions, but the average kinetic energy of the molecules does not change with time, as long as the temperature of the gas remains constant
5. The average kinetic energy of the molecules is proportional to absolute temperature. At any given temperature, the molecules of all gases have the same average kinetic energy

The pressure of a gas is caused by collisions of molecules with the walls of the container. The magnitude of the pressure is determined by how often and how "hard" the molecules strike the walls.

If two different gases are at the same temperature, they have the same average kinetic energy. If the temperature of a gas is doubled, its kinetic energy also doubles. Hence, molecular motion increases with increasing temperature.

- **Root-mean-square (rms) speed**: the square root of the squared speeds of the gas molecules in a gas sample. This quantity is the speed of a molecule possessing average kinetic energy.

The rms speed is important because the average kinetic energy of the gas molecules, \(\langle \epsilon \rangle\), is related directly to \(\langle u^2 \rangle\):

\[ \langle \epsilon \rangle = \frac{1}{2} m \langle u^2 \rangle \]

where \(\langle m \rangle\) is the mass of the molecule.

Because mass doesn’t change with temperature, the rms speed (and also the average speed) of molecules must increase as temperature increases.

**Applications to the Gas Laws**

1. *Effect of a volume increase at constant temperature*: If the volume is increased, the molecules must move a longer...
distance between collisions. Consequently, there are fewer collisions per unit time with the container walls, and pressure decreases.

2. **Effect of a temperature increase at constant volume**: An increase in temperature means an increase in the average kinetic energy of the molecules. If there is no change in volume, there will be more collisions with the walls per unit time. Furthermore, the molecules strike harder, hence explaining how the observed pressure increases.

### 10.8: Molecular Effusion and Diffusion

*Diffusion* is the gradual mixing of gases to form a sample of uniform composition even in the absence of mechanical agitation. In contrast, *effusion* is the escape of a gas from a container through a tiny opening into an evacuated space. The rate of effusion of a gas is inversely proportional to the square root of its molar mass (Graham’s law), a relationship that closely approximates the rate of diffusion. As a result, light gases tend to diffuse and effuse much more rapidly than heavier gases.

A gas composed of light gas particles will have the same average kinetic energy as one composed of much heavier particles, provided that the two gases are at the same temperature. The mass, \(m\), of the particles in the lighter gas is smaller that that in the heavier gas. Consequently, the particles of the lighter gas must have a higher rms speed, \(u\), than the heavier one:

\[
u = \sqrt{\frac{3RT}{M}}
\]

Since \(M\) is in the denominator, the less massive the gas molecules, the higher the rms speed

- **Effusion**: the escape of a gas through an orifice or hole. The rate of effusion depends on the molecular mass of the gas.
- **Diffusion**: the spreading of one substance through a space or through another substance

**Graham’s Law of Effusion**

- **Graham’s law**: law stating that the rate of effusion of a gas is inversely proportional to the square root of its molecular weight

\[
\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}
\]

where \(r\) is the rate of effusion

- The rate of effusion is also directly proportional to the rms speed of the molecules. This is because the only way for the molecule to escape is to "collide" with the opening. Hence, the faster the molecules are moving, the greater the likelihood that a molecule will hit the opening and effuse.

**Diffusion and Mean Free Path**

- Diffusion, like effusion, is faster for light molecules than for heavy ones. The diffusion of gases is much slower than molecular speeds because of molecular collisions. Because of these collisions, the direction of motion of a gas molecule is constantly changing, making this a slow process.
- **Mean free path**: average distance traveled by a molecule between collisions. The higher the density of a gas, the
10.9: Real Gases - Deviations from Ideal Behavior

No real gas exhibits ideal gas behavior, although many real gases approximate it over a range of conditions. Gases most closely approximate ideal gas behavior at high temperatures and low pressures. Deviations from ideal gas law behavior can be described by the van der Waals equation, which includes empirical constants to correct for the actual volume of the gaseous molecules and quantify the reduction in pressure due to intermolecular attractive forces.

The ideal gas equation may be rearranged as follows to understand deviations from ideal-gas behavior:

$$\frac{PV}{RT} = n$$

- For a mole of ideal gas (n = 1), the quantity PV / RT = 1 at all pressures. However, real gases do not behave in such a way. At high pressures, the deviation is very high, however it is less with lower pressures. In general, the deviations from ideal behavior increase as temperature decreases, becoming significant near the temperature at which the gas is converted into a liquid.
- Basic assumptions in the kinetic molecular theory suggest that molecules of an ideal gas occupy no space and have no attraction for each other. Real molecules, however, do have finite volumes, and they do attract one another.
- Also, if the volume of the container in which the gas is contained is large, the molecules have plenty of free space, and do not take much of the container’s volume itself. However, as pressure increases, the gas molecules occupy a much larger fraction of the container’s volume.
- In addition, the attractive forces between molecules come into play at short distances, as when molecules are crowded together at high pressures. Because of these attractive forces, the impact of a given molecule with the wall of the container is lessened.
- Temperature determines how effective attractive forces between gas molecules are. As the gas is cooled, the average kinetic energy decreases, while intermolecular attractions remain constant.

The Van der Waals Equation

According to the ideal gas equation:

$$P = \frac{nRT}{V}$$  \text{(ideal gas)}

According to Van der Waals:

$$P = \frac{nRT}{V - nb} - \frac{n^2a}{V^2}$$

Correction for volume of molecules – Correction for molecular attractions

- The Van der Waals constant b is a measure of the actual volume occupied by a mole of gas molecules; b has units of L/mol.
- The Van der Walls constant a has units of L$^2$-atm/mol$^2$. The magnitude of a reflects how strongly the gas molecules attract each other.

Van der Waals equation
The Van der Waals constants $a$ and $b$ are different for each gas. The values of these constants generally increase with an increase in mass of the molecule and with an increase in the complexity of its structures.