Lecture 25-27
Gases
Characteristics of Gases

• Unlike liquids and solids, gases
  – Expand to fill their containers.
  – Are highly compressible.
  – Have extremely low densities.
Pressure of a gas

• Force per unit area exerted by the gas.
  – How? By colliding with the surface of the vessel

\[ \text{F} = \text{ma} = \Delta \text{mv} \]
\[ \frac{\text{F}}{\text{A}} = \text{P} \]

Si units: Nm\(^{-2}\) Pascals, Pa.
Pressure

- **Pressure** is the amount of force applied to an area:

  \[ P = \frac{F}{A} \]

- **Atmospheric pressure** is the weight of air per unit of area.

Atmospheric pressure at Earth’s surface
Units of Pressure

• mmHg or torr
  – These units are literally the difference in the heights measured in mm ($h$) of two connected columns of mercury.

• Atmosphere
  – 1.00 atm = 760 torr
The manometer is used to measure the difference in pressure between atmospheric pressure and that of a gas in a vessel.

\[ P_{\text{gas}} = P_{\text{atm}} + P_h \]
**Manometer**

Example: What is the pressure in atmospheres of the gas in the figure?

\[ P_{\text{gas}} = 760 \text{ mm} + (136.4 - 103.8) \]
\[ = 760 \text{ mm} + 32.6 \text{ mm} = 792.6 \text{ mm} \]

792 mm (1 atm/760 mm) = 1.04 atm
Standard Pressure

• Normal atmospheric pressure at sea level is referred to as standard pressure.

• It is equal to
  – 1.00 atm
  – 760 torr (760 mmHg)
  – 101.325 kPa
**Avogadro’s Law**

- The volume of a gas at constant temperature and pressure is directly proportional to the number of moles of the gas.
- Mathematically, this means $V = kn$

<table>
<thead>
<tr>
<th></th>
<th>He</th>
<th>N$_2$</th>
<th>CH$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume</td>
<td>22.4 L</td>
<td>22.4 L</td>
<td>22.4 L</td>
</tr>
<tr>
<td>Pressure</td>
<td>1 atm</td>
<td>1 atm</td>
<td>1 atm</td>
</tr>
<tr>
<td>Temperature</td>
<td>0 °C</td>
<td>0 °C</td>
<td>0 °C</td>
</tr>
<tr>
<td>Mass of gas</td>
<td>4.00 g</td>
<td>28.0 g</td>
<td>16.0 g</td>
</tr>
<tr>
<td>Number of gas molecules</td>
<td>$6.02 \times 10^{23}$</td>
<td>$6.02 \times 10^{23}$</td>
<td>$6.02 \times 10^{23}$</td>
</tr>
</tbody>
</table>
Charles’s Law

• The volume of a fixed amount of gas at constant pressure is directly proportional to its absolute temperature.
Charles’s Law

- So, $\frac{V}{T} = k$
- A plot of $V$ versus $T$ will be a straight line.


**Boyle’s Law**

The volume of a fixed quantity of gas at constant temperature is inversely proportional to the pressure.
\( P \) and \( V \) are Inversely Proportional

A plot of \( V \) versus \( P \) results in a curve.

\[ PV = k \]

\[ V = k \left( \frac{1}{P} \right) \]

This means a plot of \( V \) versus \( 1/P \) will be a straight line.
**Ideal-Gas Equation**

• So far we’ve seen that

\[ V \propto 1/P \text{ (Boyle’s law)} \]
\[ V \propto T \text{ (Charles’ s law)} \]
\[ V \propto n \text{ (Avogadro’s law)} \]

• Combining these, we get

\[ V \propto \frac{nT}{P} \]
The constant of proportionality is known as $R$, the gas constant.

**Ideal-Gas Equation**

<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>J/mol-K*</td>
<td>8.314</td>
</tr>
<tr>
<td>cal/mol-K</td>
<td>1.987</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>

*SI unit
Ideal-Gas Equation

The relationship

\[ V \propto \frac{nT}{P} \]

then becomes

\[ V = R \frac{nT}{P} \]

or

\[ PV = nRT \]
A gas law problem

• 2.0 liters of an ideal gas is heated from 50° C to 150 °C under a constant pressure of 1 atm. What happens to the volume?

• n is constant, P is constant:
  
  \[ PV = nRT \]
  
  \[ \frac{V_{\text{init}}}{T_{\text{init}}} = \frac{nR}{P} = K = \frac{V_{\text{final}}}{T_{\text{final}}} \]

• \[ 2.0 \text{atm}/323\text{K} = \frac{V_{\text{final}}}{423\text{K}} \]

• \[ 2.0 \text{atm}(423\text{K})/323\text{K} = 2.6 \text{ liters} \]
Gas law problem

• To what must the pressure be increased (at 423 K) to reduce the volume back to its original value (2.0 L)?

• Now T and n are constant:

• $PV = nRT$, $PV = K$

• $1\text{atm}(2.6\text{L}) = P_{\text{final}}(2.0\text{L})$

• $1\text{atm}(2.6\text{L})/2.0\text{L} = 1.31 \text{ atm.}$
Dalton’s Law of Partial Pressures

• The total pressure of a mixture of gases equals the sum of the pressures that each would exert if it were present alone.

• In other words,

\[ P_{\text{total}} = P_1 + P_2 + P_3 + \ldots \]
Gases

• 3 samples of gases
• 1 liter $O_2$ at 2 atm pressure
• 2 liter $N_2$ at 1 atm pressure
• 2 liter He at 2 atm pressure
• What’s the final pressure if all are put in a 3 L container, assume T constant.
Partial pressures

- $P_i V_i = nRT = P_f V_f$
- $P_i V_i / V_f = P_f$

Oxygen: $2 \text{ atm}(1 \text{ L})/3 \text{ L} = 2/3 \text{ atm}$

Nitrogen: $1 \text{ atm}(2 \text{ L})/3 \text{ L} = 2/3 \text{ atm}$

Helium: $2(2 \text{ L})/3 \text{ L} = 4/3 \text{ atm}$

TOTAL $8/3 \text{ atm}$. 
Partial pressures

- 2 gases mix and react. Open valve, gases form as much product as possible. What is the final pressure? Assume T constant.

\[
2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2
\]

\[
\begin{align*}
4\text{L} & \quad 2\text{L} & \quad ? \\
.5\text{atm} & \quad 1\text{atm} & \quad \text{total V 6 L} \\
4\text{L}(.5\text{atm})/6 & \quad 2\text{L}(1\text{atm})/6 \\
1/3\text{atm} & \quad 1/3\text{atm}
\end{align*}
\]
\[
\begin{array}{ccc}
2\text{NO} & + & \text{O}_2 \rightarrow \\
\text{Start:} & 4\text{L} & 2 \text{L} & 0 \\
& .5 \text{ atm} & 1 \text{ atm} & \text{total V 6 L} \\
& 4\text{L}(.5 \text{ atm})/6 & 2\text{L}(1\text{ atm})/6 & \\
& 1/3 \text{ atm} & 1/3 \text{ atm} & \\
\text{End:} & 0 & 1/3/2 = 1/6 & 1/3 \\
\end{array}
\]

Total: \(1/6 \text{ atm} + 1/3 \text{ atm} = \frac{1}{2} \text{ atm}\).
Partial pressures

• Mixture of 40g each of He and O₂ at 2 atm.
• What is the partial pressure of each?

\[ PV = nRT \quad P = \frac{nRT}{V} \quad \frac{P}{n} = \frac{RT}{V} \]

\[ \frac{P_{He}}{P_{tot}} = \frac{n_{He}}{n_{tot}} \frac{RTV^{-1}}{RTV^{-1}} = \frac{n_{He}}{n_{tot}} \]

\[ P_{He} = \frac{n_{He}}{n_{tot}} (P_{tot}) \]

Moles He = 40 g/4 gmol⁻¹ = 10 mole
Moles Oxygen: 40 g/32 gmol⁻¹ = 5/4 mole

\[ n_{tot} = 11.25 \text{ moles} \]

\[ P_{He} = \frac{10}{11.25}(2\text{ atm}) \]

\[ P_{O2} = \frac{1.25 \text{ mole}}{11.25 \text{ mole}(2 \text{ atm})} = \]
Kinetic-Molecular Theory

Pressure inside container comes from collisions of gas molecules with container walls

This is a model that aids in our understanding of what happens to gas particles as environmental conditions change.
Main Tenets of Kinetic-Molecular Theory

Gases consist of large numbers of molecules that are in continuous, random motion.
Main Tenets of Kinetic-Molecular Theory

The combined volume of all the molecules of the gas is negligible relative to the total volume in which the gas is contained.
Main Tenets of Kinetic-Molecular Theory

Attractive and repulsive forces between gas molecules are negligible.

Pressure inside container comes from collisions of gas molecules with container walls.
Main Tenets of Kinetic-Molecular Theory

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.
Main Tenets of Kinetic-Molecular Theory

The average kinetic energy of the molecules is proportional to the absolute temperature.

- At 0 °C, fewer than half the molecules move at speeds greater than 500 m/s.
- At 100 °C, more than half the molecules move at speeds greater than 500 m/s.
Effusion

**Effusion** is the escape of gas molecules through a tiny hole into an evacuated space.
The difference in the rates of effusion for helium and nitrogen, for example, explains why a helium balloon would deflate faster.
Diffusion is the spread of one substance throughout a space or throughout a second substance.
Graham’s Law

\[ KE_1 = KE_2 \]

\[ \frac{1}{2} m_1 v_1^2 = \frac{1}{2} m_2 v_2^2 \]

\[ \frac{m_1}{m_2} = \frac{v_2^2}{v_1^2} \]

Diffusion rate 1
Diffusion rate 2

= \frac{m_2^{1/2}}{m_1^{1/2}}

compare H\textsubscript{2} and O\textsubscript{2}:
rate H\textsubscript{2}/rate O\textsubscript{2} =
(32)^{1/2}/2^{1/2} = 4

Hydrogen effuses or diffuses 4 times faster than oxygen
In the real world, the behavior of gases only conforms to the ideal-gas equation at relatively high temperature and low pressure.
Real Gases

Even the same gas will show wildly different behavior under high pressure at different temperatures.
Deviations from Ideal Behavior

The assumptions made in the kinetic-molecular model (negligible volume of gas molecules themselves, no attractive forces between gas molecules, etc.) break down at high pressure and/or low temperature.
Corrections for Nonideal Behavior

• The ideal-gas equation can be adjusted to take these deviations from ideal behavior into account.

• The corrected ideal-gas equation is known as the van der Waals equation.
Non ideal gases

\[ (P + \frac{n^2a}{\sqrt{2}}) (V - nb) = nRT \]

- Van der Waals equation
- \( a \) corrects for attraction of gas atoms/molecules
- \( b \) corrects for the fact that molecules have size.
The van der Waals Equation

\[(P + \frac{n^2a}{V^2})(V - nb) = nRT\]

**TABLE 10.3 • Van der Waals Constants for Gas Molecules**

<table>
<thead>
<tr>
<th>Substance</th>
<th>(a) (L(^2)-atm/mol(^2))</th>
<th>(b) (L/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0.0341</td>
<td>0.02370</td>
</tr>
<tr>
<td>Ne</td>
<td>0.211</td>
<td>0.0171</td>
</tr>
<tr>
<td>Ar</td>
<td>1.34</td>
<td>0.0322</td>
</tr>
<tr>
<td>Kr</td>
<td>2.32</td>
<td>0.0398</td>
</tr>
<tr>
<td>Xe</td>
<td>4.19</td>
<td>0.0510</td>
</tr>
<tr>
<td>H(_2)</td>
<td>0.244</td>
<td>0.0266</td>
</tr>
<tr>
<td>N(_2)</td>
<td>1.39</td>
<td>0.0391</td>
</tr>
<tr>
<td>O(_2)</td>
<td>1.36</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>
</tbody>
</table>