Skills to Develop

- Correlate energy to motion of gas molecules.
- Correlate temperature to kinetic energy of gas molecules.
- Interpret pressure in terms of gas molecule motion.
- Describe effusion rate in terms of molecular motion.
- Estimate effusion rate and time by comparison.

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**Kinetic Theory of Gases**

Temperature and pressure are macroscopic properties of gases. These properties are related to molecular motion, which is a microscopic phenomenon. The kinetic theory of gases correlates between macroscopic properties and microscopic phenomena. Kinetics means the study of motion, and in this case motions of gas molecules.

At the same temperature and volume, the same numbers of moles of all gases exert the same pressure on the walls of their containers. This is known as **Avogadro's principle**. His theory implies that the same numbers of moles of gas have the same number of molecules.

Common sense tells us that the pressure is proportional to the average kinetic energy of all the gas molecules. Avogadro's principle also implies that the kinetic energies of various gases are the same at the same temperature. The molecular masses are different from gas to gas, and if all gases have the same average kinetic energy, the average speed of a gas is unique.

Based on the above assumption or theory, **Boltzmann** (1844-1906) and **Maxwell** (1831-1879) extended the theory to imply that the average kinetic energy of a gas depends on its temperature.

They let \( u \) be the average or root-mean-square speed of a gas whose molar mass is \( M \). Since \( N \) is the Avogadro's number, the average kinetic energy is \( (1/2) \left( \frac{M}{N} \right) u^2 \) or

\[
\text{K.E.} = \frac{M}{2 N} u^2 = \frac{3 R T}{2 N} = \frac{3}{2} k T
\]

Note that \( M / N \) is the mass of a single molecule. Thus,

\[
\begin{align}
\text{u} &= \left( \frac{3k N T}{M} \right)^{1/2} \\
&= \left( \frac{3 R T}{M} \right)^{1/2}
\end{align}
\]

where \( k (= R/N) \) is the **Boltzmann constant**. Note that \( u \) so evaluated is based on the average energy of gas molecules being the same, and it is called the root-mean-square speed; \( u \) is not the average speed of gas molecules.

These formulas correlate temperature, pressure and kinetic energy of molecules. The distribution of gas speed has been studied by Boltzmann and Maxwell as well, but this is beyond the scope of this course. However, you may notice that at
the same temperature, the average speed of hydrogen gas, \(\text{H}_2\), is 4 times more than that of oxygen, \(\text{O}_2\) in order to have the same average kinetic energy.

**Calculation of Effusion Rate By Comparison**

For two gases, at the same temperature, with molecular masses \(M_1\) and \(M_2\), and average speeds \(u_1\) and \(u_2\), Boltzmann and Maxwell theory implies the following relationship:

\[
[M_1 u_1^2 = M_2 u_2^2]
\]

Thus,

\[
\frac{M_1}{M_2} = \left(\frac{u_2}{u_1}\right)^2
\]

The consequence of the above property is that the effusion rate, the root mean square speed, and the most probable speed, are all inversely proportional to the square root (SQRT) of the molar mass. Simply formulated, the Graham's law of effusion is

\[
\text{rate of effusion} = \frac{k}{\mathrm{d}^{1/2}} = \frac{k'}{\mathrm{M}^{1/2}}
\]

Have you noticed that helium balloons were usually deflated the next day while sizes of normal air balloons will keep at least for a few days? Small helium molecules not only effuse through the tiny holes of the balloons, they also effuse much faster through them.

The theories covered here enable you to make many predictions. Apply these theories to solve the following problems.

**Example 1**

Calculate the kinetic energy of 1 mole of nitrogen molecules at 300 K.

**SOLUTION**

Assume nitrogen behaves as an ideal gas, then

\[
E_{\text{kin}} = \frac{3}{2} R T
\]

\[
= \frac{3}{2} \times 8.3145 \frac{\text{J}}{\text{mol} \cdot \text{K}} \times 300 \text{ K}
\]

\[
= 3742 \text{ J/mol (or 3.74 kJ/mol)}
\]

**DISCUSSION**

At 300 K, any gas that behaves like an ideal gas has the same energy per mol.

**Example 2**

Evaluate the root-mean-square speed of \(\text{H}_2\), \(\text{He}\), \(\text{N}_2\), \(\text{O}_2\) and \(\text{CO}_2\) at 310 K (the human body temperature).
Recall that

\[
\begin{align*}
  u &= \left(\frac{3k N T}{M}\right)^{1/2} \\
  &= \left(\frac{3 R T}{M}\right)^{1/2} \\
  &= \left(\frac{3 \times 8.3145 \times 310}{0.002}\right)^{1/2} \\
  &= 1966 \text{ m/s}
\end{align*}
\]

Note that the molecular mass of hydrogen is 0.002 kg/mol. These units are used because the constant \( R \) has been calculated using the SI units. The calculation for other gases is accomplished using their molar mass in kg.

\[
\begin{align*}
  u &= \left(\frac{3k N T}{M}\right)^{1/2} \\
  &= \left(\frac{3 R T}{M}\right)^{1/2} \\
  &= \frac{(3 \times 8.3145 \times 310)^{1/2}}{M^{1/2}} \\
  &= \frac{87.9345}{M^{1/2}} \text{ m/s}
\end{align*}
\]

The root-mean-square speeds are:

<table>
<thead>
<tr>
<th>Gas</th>
<th>Molar Mass</th>
<th>((u)) (root-mean-square speed in m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H})</td>
<td>2</td>
<td>1966</td>
</tr>
<tr>
<td>(\text{He})</td>
<td>4</td>
<td>1390</td>
</tr>
<tr>
<td>(\text{H}_2)</td>
<td>28</td>
<td>525</td>
</tr>
<tr>
<td>(\text{O}_2)</td>
<td>32</td>
<td>492</td>
</tr>
<tr>
<td>(\text{CO}_2)</td>
<td>44</td>
<td>419</td>
</tr>
</tbody>
</table>

DISCUSSION

Molar masses are 349 and 352 for \(\text{UF}_6\) and \(\text{UF}_6\) respectively. Using the method above, their root-mean-square speeds are 149 and 148 m/s respectively.

The separation of these two isotopes of uranium was a necessity during the time of war for the US scientists. Gas diffusion was one of the methods employed for their separation.

Example 3

Assume air and helium molecules pass through the undetected holes in balloons with equal opportunities. If a helium balloon takes 10.0 hours to reduce its size by 5.0 \%, how long will it take a nitrogen balloon to reduce its size by 5.0 \%?
The effusion rates are

\[
\text{rate of effusion} = \frac{k}{d^{1/2}} = \frac{k'}{M^{1/2}}
\]

Let's assume an average rate of effusion of helium to be \( \frac{5}{10} = 0.5 \), then the effusion rate of nitrogen is \( 0.5 \times \left( \frac{4}{28} \right)^{1/2} = 0.189 \). The time required to effuse the same amount is thus \( 10 \times 0.5/0.189 = 26.5 \text{ hr} \).

The time required can be evaluated by

\[
\begin{align*}
time &= 10 \times \left( \frac{28}{4} \right)^{1/2} \text{ hr} \\
&= 26.5 \text{ hr}
\end{align*}
\]

Confidence Building Questions

1. **Calculate the root mean square speed of \( \text{N}_2 \) (molar mass = 28) at 37 °C (310 K, body temperature).** \( R = 8.314 \text{ kg m}^2/(\text{s}^2 \text{ mol K}) \).

   Hint: 525 m/s

   **Skill:**
   Calculate the root mean square speed \( u \) of gas molecules.

2. **Which gas has a highest root mean square speed:** \( \text{H}_2 \), \( \text{N}_2 \), \( \text{O}_2 \), \( \text{CH}_4 \), or \( \text{CO}_2 \)?

   Hint: hydrogen gas

   **Skill:**
   Knowing that \( \text{H}_2 \) has the lowest molecular mass makes your decision easy.

3. **Which gas has a lowest root mean square speed:** \( \text{H}_2 \), \( \text{N}_2 \), \( \text{O}_2 \), \( \text{CH}_4 \), or \( \text{CO}_2 \)?

   Hint: carbon dioxide

   **Skill:**
   Know that \( \text{CO}_2 \) has the highest molecular mass.

4. **Assuming ideal gas behavior, calculate the kinetic energy of 1.00 mole of \( \text{N}_2 \) at 37 °C (= 310 K).** \( R = 8.314 \text{ J/(mol K)}; \text{N}_2 \text{ molar mass} = 28.0 \)

   Hint: 3.87e3 J/mol
Skill:
Calculate the kinetic energy of any amount of any gas at any temperature.

5. **Which of the following gases has the highest effusion rate through a pinhole opening of its container (T = 300K): \(\text{He}\) (molar mass 4), \(\text{N}_2\) (28), \(\text{O}_2\) (32), \(\text{CO}_2\) (44), \(\text{SO}_2\) (64), or \(\text{Ar}\) (40)?**

   Hint: helium

Skill:
Associate effusion rate with root mean square speed, and determine the effusion rates.

6. **For which gas in the accompanying list is the effusion rate the smallest (T = 400 K): \(\text{NH}_3\) (17), \(\text{CO}_2\) (44), \(\text{Cl}_2\) (71), \(\text{CH}_4\) (16)?**

   Hint: chlorine gas

Skill:
Calculate the root mean speed for these gases. The average speed is 324 m/s for \(\text{Cl}_2\), 681 m/s for \(\text{CH}_4\).

7. **The most probable speed of \(\text{CH}_4\) (molar mass 16.0) at a given temperature is 411 m/s. What is the most probable speed of \(\text{He}\) (molar mass 4.00) at the same temperature?**

   Hint: 822 m/s

Discussion:
At the same T, the most probable speed of a gas is inversely proportional to the square-root of its molar mass.

Contributors

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