Goals for Chapter 18

- To study equations of state
- To apply the molecular properties of matter
- To consider the kinetic-molecular model of an ideal gas
- To calculate heat capacities
- To consider molecular speeds
- To study phases of matter
Introduction

• Cooking is an artistic combination of burning fuel, careful control of heat, manipulation of molecules, and creative presentation. In the figure at right, you can see some students following a lesson in these very ideas.

• We’ll study equations of state that describe the interaction of state variables like pressure, volume, and temperature.
Equations of state

• A first model for describing the behavior of a gas is the ideal-gas equation.

• Active study of gases is done by changing pressure, volume, temperature, or quantity of material and observing the result.
Changing parameters of an ideal gas—volume

• Consider Problem-Solving Strategy 18.1.

• Follow Example 18.1.
changing parameters of an ideal gas—compression

- Consider Example 18.2, compression of gas in an automobile engine.

- Figure 18.3 illustrates the example.
Solving for the quantity of material given P, V, and T

- Consider Example 18.3, the mass of air in a scuba tank.
Variation of pressure as elevation changes

- Consider Example 18.4.
- Figure 18.4 presents the results graphically.

![Graph showing variation of pressure with elevation change](image)

$p = p_0 e^{-\frac{Mg y}{RT}}$
An improvement to the equation of state

- The van der Waals equation includes corrections for the facts that molecules are not point particles, that they have volume, and for the attraction/repulsion that naturally exists between the adjacent atoms/molecules in an ensemble.

(a) An idealized model of a gas

Gas molecules are infinitely small.

They exert forces on the walls of the container but not on each other.

(b) A more realistic model of a gas

Gas molecules have volume, which reduces the volume in which they can move.

They exert attractive forces on each other, which reduces the pressure ...

... and they exert forces on the container’s walls.
Δ(PV) curves at constant temperature— isotherms

- A single experiment can measure how pressure changes as volume changes. This is an isothermal curve.

- Many isothermal curves together make a three-dimensional phase surface.

Each curve represents pressure as a function of volume for an ideal gas at a single temperature. For each curve, $pV$ is constant and is directly proportional to $T$ (Boyle’s law).

Above the critical temperature $T_c$ there is no liquid–vapor phase transition.

Below $T_c$, the material condenses to liquid as it is compressed.

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Molecular properties of matter

- Just for perspective, the amount of carbon in the graphite of just one #2 pencil represents $10^{23}$ carbon atoms.

- Each adjacent atom (or molecule) in a sample will experience forces from its “neighbors.” These forces range in strength over several orders of magnitude.

- Follow Example 18.5.
Microscopes can now resolve individual atoms

- For centuries, evidence of individual atoms was clever inference from macroscopic measurements.
- Scanning or tunneling electron microscopy is now able to resolve objects of atomic and molecular size.
Atomic/molecular collisions and pressure

- The kinetic-molecular theory relates pressure to elastic collisions between individual particles and the walls of the container.

- Even though atoms/molecules are light, they move at hundreds or even thousands of m/s, and each contributes significant kinetic energy.

- Refer to Problem-Solving Strategy 18.2.

- Follow Example 18.6.

- Follow Example 18.7.
How often do atoms/molecules collide?

- If the size of each particle is determined to be of radius $r$, the space they present to other particles as a target can be calculated.

- A good example to demonstrate this “target” a molecule presents is to depict an atom as a basketball and roll two of them around one another. You can visualize how far apart they must remain to avoid collision.

- The distance an atom/molecule will travel without a collision is termed the “mean free path.”

- Follow Example 18.8.
How much heat energy can ensembles contain?

- An atom can absorb energy as the kinetic energy of its motion.
- A molecule can absorb energy in its translation, and also in its rotation and in the vibrations of one atom in its structure with respect to the others.
- Atomic/molecular energy absorbed is termed its “heat capacity.”

### Table 18.1 Molar Heat Capacities of Gases

<table>
<thead>
<tr>
<th>Type of Gas</th>
<th>Gas</th>
<th>$C_v$ (J/mol · K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monatomic</td>
<td>He</td>
<td>12.47</td>
</tr>
<tr>
<td></td>
<td>Ar</td>
<td>12.47</td>
</tr>
<tr>
<td>Diatomic</td>
<td>H$_2$</td>
<td>20.42</td>
</tr>
<tr>
<td></td>
<td>N$_2$</td>
<td>20.76</td>
</tr>
<tr>
<td></td>
<td>O$_2$</td>
<td>21.10</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>20.85</td>
</tr>
<tr>
<td>Polyatomic</td>
<td>CO$_2$</td>
<td>28.46</td>
</tr>
<tr>
<td></td>
<td>SO$_2$</td>
<td>31.39</td>
</tr>
<tr>
<td></td>
<td>H$_2$S</td>
<td>25.95</td>
</tr>
</tbody>
</table>
Illustration of heat absorption into degrees of freedom

(a) **Translational motion.** The molecule moves as a whole; its velocity may be described as the x-, y-, and z-velocity components of its center of mass.

(b) **Rotational motion.** The molecule rotates about its center of mass. This molecule has two independent axes of rotation.

(c) **Vibrational motion.** The molecule oscillates as though the nuclei were connected by a spring.

Below 50 K, H₂ molecules undergo translation but do not rotate or vibrate. Appreciable rotational motion begins to occur above 50 K. Appreciable vibrational motion begins to occur above 600 K.
Measuring atomic/molecular speeds

- Beams of molecules are created in a vacuum chamber where the pressure is low enough to have a mean free path at least $10 \times$ farther than the sample path. (A typical apparatus would require $10^{-6}$ torr to obtain mean free path $\sim 10$–100 m and accommodate a 1 m experimental setup.)
Molecules form distributions of velocities

- A temperature-dependent distribution forms around the most likely velocity for a given sample.

**Table 18.2** Fractions of Molecules in an Ideal Gas with Speeds Less than Various Multiples of $v/v_{\text{rms}}$

<table>
<thead>
<tr>
<th>$v/v_{\text{rms}}$</th>
<th>Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>0.011</td>
</tr>
<tr>
<td>0.40</td>
<td>0.077</td>
</tr>
<tr>
<td>0.60</td>
<td>0.218</td>
</tr>
<tr>
<td>0.80</td>
<td>0.411</td>
</tr>
<tr>
<td>1.00</td>
<td>0.608</td>
</tr>
<tr>
<td>1.20</td>
<td>0.771</td>
</tr>
<tr>
<td>1.40</td>
<td>0.882</td>
</tr>
<tr>
<td>1.60</td>
<td>0.947</td>
</tr>
<tr>
<td>1.80</td>
<td>0.979</td>
</tr>
<tr>
<td>2.00</td>
<td>0.993</td>
</tr>
</tbody>
</table>

As temperature increases:
- the curve flattens.
- the maximum shifts to higher speeds.
The positions of (s), (l), and (g) are plotted on phase diagrams.

- Lines are drawn for freezing, melting, and boiling curves on a pT axis.

**Table 18.3 Triple-Point Data**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Temperature (K)</th>
<th>Pressure (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>13.80</td>
<td>$0.0704 \times 10^5$</td>
</tr>
<tr>
<td>Deuterium</td>
<td>18.63</td>
<td>$0.171 \times 10^5$</td>
</tr>
<tr>
<td>Neon</td>
<td>24.56</td>
<td>$0.432 \times 10^5$</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>63.18</td>
<td>$0.125 \times 10^5$</td>
</tr>
<tr>
<td>Oxygen</td>
<td>54.36</td>
<td>$0.00152 \times 10^5$</td>
</tr>
<tr>
<td>Ammonia</td>
<td>195.40</td>
<td>$0.0607 \times 10^5$</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>216.55</td>
<td>$5.17 \times 10^5$</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>197.68</td>
<td>$0.00167 \times 10^5$</td>
</tr>
<tr>
<td>Water</td>
<td>273.16</td>
<td>$0.00610 \times 10^5$</td>
</tr>
</tbody>
</table>
P, V, and T may all be plotted to form 3-D surfaces
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