Atomic and molecular masses are measured in unified atomic mass units (u). This unit is defined so that the carbon-12 atom has a mass of exactly 12.0000 u. Expressed in kilograms:

\[ 1 \text{ u} = 1.6605 \times 10^{-27} \text{ kg} \]

Brownian motion is the jittery motion of tiny flecks in water; these are the result of collisions with individual water molecules.

On a microscopic scale, the arrangements of molecules in solids (a), liquids (b), and gases (c) are quite different.
Temperature and Thermometers

Temperature is a measure of how hot or cold something is. Most materials expand when heated.

Thermometers are instruments designed to measure temperature. In order to do this, they take advantage of some property of matter that changes with temperature.

Common thermometers used today include the liquid-in-glass type and the bimetallic strip.

Temperature is generally measured using either the Fahrenheit or the Celsius scale. The freezing point of water is 0°C, or 32°F; the boiling point of water is 100°C, or 212°F.

Kelvin Scale

- When the pressure of a gas goes to zero, its temperature is $-273.15{}^\circ C$
- This temperature is called absolute zero
- This is the zero point of the Kelvin scale
  $-273.15{}^\circ C = 0 K$
- To convert: $T_C = T_K - 273.15$
  - The size of the degree in the Kelvin scale is the same as the size of a Celsius degree
Comparing Temperature Scales

<table>
<thead>
<tr>
<th>Steam point</th>
<th>100°C</th>
<th>212°F</th>
<th>373.15 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ice point</td>
<td>0°C</td>
<td>32°F</td>
<td>273.15 K</td>
</tr>
</tbody>
</table>

Celsius | Fahrenheit | Kelvin |

Converting Among Temperature Scales

\[ T_C = T_K - 273.15 \]
\[ T_F = \frac{9}{5} T_C + 32 \]
\[ T_C = \frac{5}{9} (T_F - 32) \]
\[ \Delta T_F = \frac{9}{5} \Delta T_C \]

Thermal Equilibrium and the Zeroth Law of Thermodynamics

Two objects placed in thermal contact will eventually come to the same temperature. When they do, we say they are in thermal equilibrium.

The Zeroth law of thermodynamics says that if two objects are each in equilibrium with a third object, they are also in thermal equilibrium with each other.

Thermal Expansion

- The thermal expansion of an object is a consequence of the change in the average separation between its constituent atoms or molecules.
- At ordinary temperatures, molecules vibrate with a small amplitude.
- As temperature increases, the amplitude increases.
  - This causes the overall object as a whole to expand.

Linear expansion occurs when an object is heated.

\[ L = L_0 (1 + \alpha \Delta T) \]

Here, \( \alpha \) is the coefficient of linear expansion.

Volume expansion is similar, except that it is relevant for liquids and gases as well as solids:

\[ \Delta V = \beta V_0 \Delta T \]

Here, \( \beta \) is the coefficient of volume expansion. For uniform solids, \( \beta \approx 3\alpha \).
Example 1: Bridge Expansion
The steel bed of a suspension bridge is 200 m long at 20°C. If the extremes of temperature to which it might be exposed are −30°C to 40°C, how much will it contract and expand?

\[ \Delta L = (12 \times 10^{-6} / ^\circ C)(200m)(40^\circ C - 20^\circ C) = 4.8 \times 10^{-2} m \]  
expand

\[ \Delta L = (12 \times 10^{-6} / ^\circ C)(200m)(-50^\circ C) = -12.0 \times 10^{-2} m \]  
contract

Example 2: A steel railroad track has a length of 30,000 m when the temperature is 0°C. What is its length on a hot day when the temperature is 40°C? If the track can’t move what is the stress in the track due to the temperature change?

a) \[ \Delta L = \alpha L_o \Delta T = [11 \times 10^{-6} (^\circ C)^{-1}](40.0^\circ C) = 0.013 m \quad L = L_o + \Delta L = 30.013 m \]

b) \[ \frac{F}{A} = Y \frac{\Delta L}{L} = (2.00 \times 10^{11} Pa)(\frac{0.013 m}{30.0 m}) = 8.67 \times 10^7 Pa \]

Example 3: Ring on a Rod
An iron ring is to fit snugly on a cylindrical iron rod. At 20°C, the diameter of the rod is 6.445 cm and the inside diameter of the ring is 6.420 cm. To slip over the rod, the ring must be slightly larger than the rod diameter by about 0.008 cm. To what temperature must the ring be brought if its hole is to be large enough so it will slip over the rod?

\[ \Delta T = \frac{\Delta L}{\alpha L_o} = \frac{6.453 cm - 6.420 cm}{(12 \times 10^{-6} C^{-1})(6.420 cm)} = 430^\circ C \]

So it must be raised at least to: \[ T = (20^\circ C + 430^\circ C) = 450^\circ C \]

Example 4: Gas tank in the sun
The 70-L steel gas tank of a car is filled to the top with gasoline at 20°C. The car is then left to sit in the sun, and the tank reaches a temperature of 40°C. How much gasoline do you expect to overflow from the tank?

The gasoline expands: \[ \Delta V = \beta V_o \Delta T = (950 \times 10^{-6} C^{-1})(70 L)(20^\circ C) = 1.3 L \]

The tank increases in volume by: \[ \Delta V = (36 \times 10^{-6} C^{-1})(70 L)(20^\circ C) = 0.050 L \]
Water behaves differently from most other solids – its minimum volume occurs when its temperature is 4°C. As it cools further, it expands, as anyone who has left a bottle in the freezer to cool and then forgets about it can testify.

Example 5: Global Warming and Coastal Flooding
Estimate the fractional change in the volume of Earth’s oceans due to an average temperature change of 1°C. Use the fact that the average depth of the ocean is $4.00 \times 10^3 \text{m}$ to estimate the change in depth. Note that $\beta_{\text{water}} = 2.07 \times 10^{-4} (°C)^{-1}$

a) Find the fractional change in volume

Divide the volume expansion equation by $V_o$ and substitute

$$\frac{\Delta V}{V_o} = \beta \Delta T = (2.07 \times 10^{-4} (°C)^{-1}) = 2 \times 10^{-4}$$

b) Find the approximate increase in depth

$$\Delta L = \alpha L_o \Delta T = \left(\frac{\beta}{3}\right) L_o \Delta T = \Delta L = 6.90 \times 10^{-5} (°C)^{-1}(4000 \text{m})(1° \text{C}) \approx 0.3 \text{m}$$

Unusual Behavior of Water

- As the temperature of water increases from 0°C to 4°C, it contracts and its density increases
- Above 4°C, water exhibits the expected expansion with increasing temperature
- Maximum density of water is 1000 kg/m³ at 4°C

Thermal Stresses

A material may be fixed at its ends and therefore be unable to expand when the temperature changes. It will then experience large compressive or tensile stress – thermal stress – when its temperature changes. The force required to keep the material from expanding is given by:

$$\Delta L = \frac{1}{E} \frac{F}{A} L_o$$
where \( E \) is the Young’s modulus of the material. Therefore, the stress is:

\[
F = \alpha \Delta TEA
\]

**Example 6:** Stress in concrete on a hot day
A highway is to be made of blocks of concrete 10 m long placed end to end with no space in between them to allow for expansion. If the blocks were placed at a temperature of \( 10^\circ C \), what force of compression would occur if the temperature reached \( 40^\circ C \)? The contact area between each block is 0.20 m. Will fracture occur?

\[
F = \alpha \Delta TEA = (12 \times 10^{-6} / C^\circ) (30C^\circ) (20 \times 10^9 N/m^2) (0.20m^2) = 1.4 \times 10^6 N
\]

The stress, \( F/A \) is

\[
\frac{(1.4 \times 10^6 N)}{(0.20m^2)} = 7.0 \times 10^6 N/m^2
\]

This is not far from the ultimate strength of concrete.

**Ideal Gas**

- A gas does not have a fixed volume or pressure
- In a container, the gas expands to fill the container
- Most gases at room temperature and pressure behave approximately as an ideal gas

**Characteristics of an Ideal Gas**

- Collection of atoms or molecules that move randomly
- Exert no long-range force on one another
- Each particle is individually point-like
  - Occupying a negligible volume

**Moles**

- It’s convenient to express the amount of gas in a given volume in terms of the number of moles, \( n \)

\[
n = \frac{\text{mass}}{\text{molar mass}}
\]

- One mole is the amount of the substance that contains as many particles as there are atoms in 12 g of carbon-12
  
  For example, the number of moles in 132 g of CO2 is

\[
n = \frac{132 g}{44 g/mol} = 3.0 \text{mol}.
\]

This proportion can be written as an equation:

\[
PV = nRT
\]
Ideal Gas Law

- $PV = n \ R \ T$
  - $R$ is the Universal Gas Constant
  - $R = 8.31 \text{ J/mole} \cdot \text{K}$
  - $R = 0.0821 \text{ L} \cdot \text{atm/mole} \cdot \text{K}$
- Is the equation of state for an ideal gas

The Gas Laws and Absolute Temperature

The relationship between the volume, pressure, temperature, and mass of a gas is called an equation of state.

We will deal here with gases that are not too dense.

**Boyle’s Law:** The volume of a given amount of gas is inversely proportional to the pressure as long as the temperature is constant.

\[ V \propto \frac{1}{P} \]

The volume is linearly proportional to the temperature, as long as the temperature is somewhat above the condensation point and the pressure is constant:

Extrapolating, the volume becomes zero at $-273.15^\circ C$; this temperature is called absolute zero.

**Problem Solving with the Ideal Gas Law**

Useful facts and definitions:
- Standard temperature and pressure (STP)
  \[ T = 273 \text{ K} \quad (0^\circ C) \]
  \[ P = 1.00 \text{ atm} = 1.013 \times 10^5 \text{ N/m}^2 = 101.3 \text{ kPa} \]
- Volume of 1 mol of an ideal gas is 22.4 L
- If the amount of gas does not change:
  \[ \frac{P_1 \ V_1}{T_1} = \frac{P_2 \ V_2}{T_2} \]
Always measure $T$ in kelvins
$P$ must be the absolute pressure

**Example 7:** Volume of one mol at STP
Determine the volume of 1.00 mol of any gas at STP, assuming it behaves like an ideal gas.

$$V = \frac{nRT}{P} = \frac{(1.00 \text{ mol})(8.315 \text{ J/mol} \cdot \text{K})(273 \text{ K})}{(1.013 \times 10^5 \text{ N/m}^2)} = 22.4 \times 10^{-3} \text{ m}^3$$

Since 1 liter is $1000 \text{ cm}^3 = 1 \times 10^{-3} \text{ m}^3$, 1 mol of any gas has a volume of 22.4 L at STP

**Example 8:** The mass of gas
A flexible container of oxygen ($\text{O}_2$, molecular mass = 32u) at STP has a volume of $10.0 \text{ m}^3$. What is the mass of gas enclosed?

$$n = \frac{10.0 \text{ m}^3}{22.4 \times 10^{-3} \text{ m}^3 / \text{mol}} = 446 \text{ mol}.$$  

Since 1 mol has a mass of 0.0320 kg, the mass of oxygen is

$$m = (446 \text{ mol})(0.0320 \text{ kg/mol}) = 14.3 \text{ kg}$$

**Ideal Gas Law in Terms of Molecules: Avogadro’s Number**

Since the gas constant is universal, the number of molecules in one mole is the same for all gases. That number is called Avogadro’s number:

$$N_A = 6.02 \times 10^{23}$$

The number of molecules in a gas is the number of moles times Avogadro’s number:

$$N = nN_A$$

**Kinetic Theory and the Molecular Interpretation of Temperature**

- The molecules interact only by short-range forces during elastic collisions
- The molecules make elastic collisions with the walls
- The gas under consideration is a pure substance, all the molecules are identical

**Pressure of an Ideal Gas**

- The pressure is proportional to the number of molecules per unit volume and to the average translational kinetic energy of a molecule
• The pressure is proportional to the number of molecules per unit volume and to the average translational kinetic energy of the molecule
• Pressure can be increased by
  – Increasing the number of molecules per unit volume in the container
  – Increasing the average translational kinetic energy of the molecules
• Increasing the temperature of the gas

Example 9: The ideal gas law to analyze a system of gas.
An ideal gas at $20^\circ C$ and a pressure of $1.50 \times 10^5 \text{ Pa}$ is in a container having a volume of 1.00L.

a) Determine the number of moles of gas in the container:

$$PV = nRT$$

$$n = \frac{PV}{RT} = \frac{(1.50 \times 10^5 \text{ Pa})(1.00 \times 10^{-3} \text{ m}^3)}{(8.31 J / \text{ mol} \cdot \text{K})(293 \text{ K})} = 6.61 \times 10^{-2} \text{ mol}$$

b) The gas pushes against a piston, expanding to twice its original volume, while the pressure falls to atmospheric pressure. Find the temperature after the gas expands to 2.00 L. Divide the ideal gas law for the final state by the ideal gas law for the initial state.

$$\frac{P_fV_f}{P_iV_i} = \frac{nR}{nR}$$

$$T_f = \frac{P_fV_f}{P_iV_i} T_i = \frac{(1.01 \times 10^5 \text{ Pa})(2.00L)}{(1.50 \times 10^5 \text{ Pa})(1.00L)(293 \text{ K})} = 395 \text{ K}$$

Kinetic Theory and the Molecular Interpretation of Temperature – cont.

Assumptions of kinetic theory:
• large number of molecules, moving in random directions with a variety of speeds
• molecules are far apart, on average
• molecules obey laws of classical mechanics and interact only when colliding
• collisions are perfectly elastic

• Temperature is proportional to the average kinetic energy of the molecules

$$\frac{1}{2}mv^2 = \frac{3}{2}k_BT$$

• The total kinetic energy is proportional to the absolute temperature

$$KE_{\text{total}} = \frac{3}{2}nRT$$

Example 10: Molecular KE
What is the average translational kinetic energy of molecules in a gas at $37^\circ C$?

$$KE = \frac{3}{2}kT = \frac{3}{2} (1.38 \times 10^{-23} J / K)(310K) = 6.42 \times 10^{-21} J$$
Internal Energy

- In a monatomic gas, the KE is the only type of energy the molecules can have
  \[ U = \frac{3}{2} nRT \]
- U is the *internal energy* of the gas
- In a polyatomic gas, additional possibilities for contributions to the internal energy are rotational and vibrational energy in the molecules

Speed of the Molecules

- Expressed as the *root-mean-square* (rms) speed
  \[ v_{rms} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{M}} \]
- At a given temperature, lighter molecules move faster, on average, than heavier ones
  - Lighter molecules can more easily reach escape speed from the earth

**Example 11**: Speeds of air molecules
What is the rms speed of air molecules (O\(_2\) and N\(_2\)) at room temperature (20\(^\circ\)C)?

\[
m(O_2) = (32)(1.67 \times 10^{-27} \text{ kg}) = 5.3 \times 10^{-26} \text{ kg} \\
m(N_2) = (28)(1.68 \times 10^{-27} \text{ kg}) = 4.7 \times 10^{-26} \text{ kg}
\]

Thus for oxygen

\[
v_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{(3)(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K})}{(5.3 \times 10^{-26} \text{ kg})}} = 480 \text{ m/s}
\]

For nitrogen \(v = 510 \text{ m/s}\) (about 1000 mi/hr)

**Example 12**: Armageddon!
A comet half a km in radius consisting of ice at 273K hits Earth at a speed of \(4 \times 10^4 \text{ m/s}\) (assume that all KE converts to thermal energy on impact and all thermal energy goes into warming the comet).

a) Calculate the volume and mass of the ice.

\[
V = \frac{4}{3} \pi r^3 = \frac{4}{3}(3.14)(500 \text{ m})^3 = 5.23 \times 10^8 \text{ m}^3 \\
m = \rho V = (917 \text{ kg/m}^3)(5.23 \times 10^8 \text{ m}^3) = 4.80 \times 10^{11} \text{ kg}
\]

b) Use conservation of energy to find the final temperature of the comet material.
The first three terms are negligible compared to the KE.

\[
\frac{1}{2}v^2 = \frac{1}{2}(4.00 \times 10^4 \text{ m/s})^2 = 2010 \text{ J/Kg} \cdot \text{K}
\]

\[
T = \frac{1}{c_{\text{steam}}} + 373K = \frac{1}{2} + 373K = 3.98 \times 10^5 \text{ K}
\]

c) Assuming the steam retains a spherical shape and has the same initial volume as the comet, calculate the pressure of the steam using the ideal gas law. This law actually doesn’t apply to a system at such high pressure and temperature, but can be used to get an estimate.

\[
n = (4.80 \times 10^{11} \text{ kg})(\frac{1 \text{ mol}}{0.018 \text{ kg}}) = 2.67 \times 10^{15} \text{ mol}
\]

\[
P = \frac{nRT}{V} = \frac{(2.67 \times 10^{13} \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(3.98 \times 10^5 \text{ K})}{5.23 \times 10^{8} \text{ m}^3} = 1.69 \times 10^{11} \text{ Pa}
\]

several 100 x greater than shear stress of steel

Real Gases and Changes of Phase

The curves here represent the behavior of the gas at different temperatures. The cooler it gets, the farther the gas is from ideal.

In curve D, the gas becomes liquid; it begins condensing at (b) and is entirely liquid at (a). The point (c) is called the critical point.

Below the critical temperature, the gas can liquefy if the pressure is sufficient; above it, no amount of pressure will suffice.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Critical Temperature</th>
<th>Critical Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>°C</td>
<td>K</td>
</tr>
<tr>
<td>Water</td>
<td>374</td>
<td>647</td>
</tr>
<tr>
<td>CO₂</td>
<td>31</td>
<td>304</td>
</tr>
<tr>
<td>Oxygen</td>
<td>−118</td>
<td>155</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>−147</td>
<td>126</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>−239.9</td>
<td>33.3</td>
</tr>
<tr>
<td>Helium</td>
<td>−267.9</td>
<td>5.3</td>
</tr>
</tbody>
</table>
A *PT* diagram is called a phase diagram; it shows all three phases of matter. The solid-liquid transition is melting or freezing; the liquid-vapor one is boiling or condensing; and the solid-vapor one is sublimation.

The triple point is the only point where all three phases can coexist in equilibrium.

**Phase diagram of water**

**Phase diagram of carbon dioxide**

**Vapor Pressure and Humidity**

An open container of water can evaporate, rather than boil, away. The fastest molecules are escaping from the water’s surface, so evaporation is a cooling process as well.

The inverse process is called condensation.

When the evaporation and condensation processes are in equilibrium, the vapor just above the liquid is said to be saturated, and its pressure is the saturated vapor pressure.

<table>
<thead>
<tr>
<th>Saturated Vapor Pressure of Water</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>Sat. (cm Hg)</td>
</tr>
<tr>
<td>0</td>
<td>0.76</td>
</tr>
<tr>
<td>1</td>
<td>0.78</td>
</tr>
<tr>
<td>2</td>
<td>0.81</td>
</tr>
<tr>
<td>3</td>
<td>0.84</td>
</tr>
<tr>
<td>4</td>
<td>0.87</td>
</tr>
<tr>
<td>5</td>
<td>0.90</td>
</tr>
<tr>
<td>6</td>
<td>0.93</td>
</tr>
<tr>
<td>7</td>
<td>0.96</td>
</tr>
<tr>
<td>8</td>
<td>0.99</td>
</tr>
<tr>
<td>9</td>
<td>1.02</td>
</tr>
<tr>
<td>10</td>
<td>1.05</td>
</tr>
</tbody>
</table>

The saturated vapor pressure increases with temperature.
A liquid boils when its saturated vapor pressure equals the external pressure.

Partial pressure is the pressure each component of a mixture of gases would exert if it were the only gas present. The partial pressure of water in the air can be as low as zero, and as high as the saturated vapor pressure at that temperature. Relative humidity is a measure of the saturation of the air.

\[
\text{Relative humidity} = \frac{\text{partial pressure of } H_2O}{\text{saturated vapor pressure of } H_2O} \times 100\% 
\]

When the humidity is high, it feels muggy; it is hard for any more water to evaporate. The dew point is the temperature at which the air would be saturated with water. If the temperature goes below the dew point, dew, fog, or even rain may occur.

**Diffusion**

Even without stirring, a few drops of dye in water will gradually spread throughout. This process is called diffusion.
Diffusion occurs from a region of high concentration towards a region of lower concentration.

The rate of diffusion is given by:

\[ J = DA \frac{C_1 - C_2}{\Delta x} \]

In this equation, \( D \) is the diffusion constant.

<table>
<thead>
<tr>
<th>Diffusing Molecules</th>
<th>Medium</th>
<th>( D ) (m(^2)/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2 )</td>
<td>Air</td>
<td>( 6.3 \times 10^{-5} )</td>
</tr>
<tr>
<td>( \text{O}_2 )</td>
<td>Air</td>
<td>( 1.8 \times 10^{-5} )</td>
</tr>
<tr>
<td>( \text{O}_2 )</td>
<td>Water</td>
<td>( 100 \times 10^{-11} )</td>
</tr>
<tr>
<td>Blood hemoglobin</td>
<td>Water</td>
<td>( 6.9 \times 10^{-11} )</td>
</tr>
<tr>
<td>Glycine (an amino acid)</td>
<td>Water</td>
<td>( 95 \times 10^{-11} )</td>
</tr>
<tr>
<td>DNA (mass ( 6 \times 10^8 ) u)</td>
<td>Water</td>
<td>( 0.13 \times 10^{-11} )</td>
</tr>
</tbody>
</table>