Chapter 7

Gases, liquids, and solids

Water coexisting in three states

\( \text{H}_2\text{O}_\text{(g)} \) in air
\( \text{H}_2\text{O}_\text{(l)} \) ocean
\( \text{H}_2\text{O}_\text{(s)} \) iceberg
What’s crack – a – lackin’?

- Kinetic-molecular theory of gases
- Physical states and the factors that determine them
- Gas laws
  - Boyle’s Law
  - Charles’ Law
  - Combined gas law
  - Ideal gas equation
- Evaporation of liquids
- Vapor pressure
- Boiling point
- Intermolecular forces in liquids
The kinetic molecular theory of matter

• It is easy to distinguish solids, liquids, and gases, using the following characteristics:
  – Volume/shape
  – Density
  – **Thermal expansion**: a measure of the change in volume of a sample of matter resulting from a temperature change
  – **Compressibility**: a measure of the change in the volume of a sample of matter resulting from a pressure change
Gases are fairly compressible; liquids and solids are not very compressible.
# The kinetic molecular theory of matter

<table>
<thead>
<tr>
<th>Property</th>
<th>Solid State</th>
<th>Liquid State</th>
<th>Gaseous State</th>
</tr>
</thead>
<tbody>
<tr>
<td>volume and shape</td>
<td>definite volume and definite shape</td>
<td>definite volume and indefinite shape; takes the shape of its container to the extent that it is filled</td>
<td>indefinite volume and indefinite shape; takes the volume and shape of the container that it completely fills</td>
</tr>
<tr>
<td>density</td>
<td>high</td>
<td>high, but usually lower than corresponding solid</td>
<td>low</td>
</tr>
<tr>
<td>compressibility</td>
<td>small</td>
<td>small, but usually greater than corresponding solid</td>
<td>large</td>
</tr>
<tr>
<td>thermal expansion</td>
<td>very small: about 0.01% per °C</td>
<td>small: about 0.10% per °C</td>
<td>moderate: about 0.30% per °C</td>
</tr>
</tbody>
</table>

![Diagram](image-url)
The kinetic molecular theory of matter

• The physical behavior of the three states of matter (solids, liquids, gases) can be explained by a set of five statements, called kinetic molecular theory, the basic idea being that particles that make up any substance are continually in random motion.

  – 1) Matter is composed of tiny particles (atoms, ions, or molecules) that have definite and characteristic sizes (volume, mass) that do not change
  – 2) The particles in a substance are in constant, random motion, and therefore possess kinetic energy (the energy an object possesses because of its motion)
  – 3) Particles interact with one another through attractions and repulsions, and therefore possess potential energy (the energy that matter possesses by virtue of its position, condition, and/or composition). The most significant potential energy we’ll consider in most exercises is electrostatic attraction.
  – 4) The kinetic energy of the particles in a substance increase in proportion to an increase in the absolute temperature
  – 5) Particles in a substance transfer energy to other particles in the substance through elastic collisions
The kinetic molecular theory of matter

- Potential and kinetic energies of the particles that make up a substance are what determines the physical state of that substance (solid, liquid, or gas)
  - Kinetic energy results from particles’ motions and can be thought of as a **disruptive force** that tends to cause particles to behave increasingly independently
  - Potential energy that exists between particles can be thought of as **cohesive**, yielding more ordered systems

The physical state of matter is determined by which of these two forces (disruptive or cohesive) is greater.

At **higher** temperatures, disruptive forces are greater.
At **lower** temperatures, cohesive forces are greater.
The kinetic molecular theory of matter

• Kinetic energy is temperature-dependent, so as temperature increases, the particles that make up a substance tend to move increasingly independently.

The physical state of matter is determined by which of these two forces (disruptive or cohesive) is greater.

At higher temperatures, disruptive forces are greater.
At lower temperatures, cohesive forces are greater.
Kinetic molecular theory and physical states

- Particles in **solids** are dominated by the cohesive forces that exist between them. This draws the particles close together so that they occupy fixed positions (can still vibrate as a result of kinetic energy).
Kinetic molecular theory and physical states

• In liquids, disruptive (kinetic energy) and cohesive (potential energy) forces are of about the same magnitude.

• Particles (molecules, atoms, ions) remain closely packed, but are capable of motion (random), moving past other particles but not with enough energy to become separated from other particles nearby.
Kinetic molecular theory and physical states

• Gases are characterized by complete dominance of disruptive forces (kinetic energy) over cohesive (potential energy) forces, resulting in a state in which the particles behave independently of one another.
Gas law variables

• Gas behavior is described reasonably well by simple quantitative relationships called gas laws, which describe, in mathematical terms, relationships between the pressure and temperature that a gas is subjected to, as well as the volume the gas occupies.

• The gas laws will involve the use of conversion factors that will typically involve combinations of the following units:
  – Moles, mol
  – Liters, L (milliliters, mL)
  – Kelvin, K
  – Millimeters of mercury in a barometer (mm Hg, also called torr)

Four variables are needed to completely discuss a gas: pressure, temperature, volume, and amount of gas
Gas law variables

- Pressure is a key descriptor of a gas. The pressure that a gas generates results from collisions of gas molecule with the walls of the container the gas occupies.

- These collisions create a force, which is distributed over a surface area:

$$P(\text{pressure}) = \frac{F(\text{force})}{A(\text{area})}$$

1 mm Hg = 1 torr

760 mm Hg = 1 atm = 14.7 psi  
(pounds-per-square-inch)

At sea-level, atmospheric pressure is 760 mm Hg (or 1 atmosphere)
Gas law variables

How atmospheric pressure is determined

760 mm Hg = 1 atm = 14.7 psi
Gas law variables

• Standard procedure for reporting pressures reading barometers is to record the pressure to the nearest mm Hg. Thus, when you see pressures reported in the text as 750 mm Hg or 700 mm Hg, the uncertainty in the number is in the “ones column”

• These figures are understood to have three significant digits.
Boyle’s law: a pressure-volume relationship

- Boyle’s law states that the volume of a fixed amount of gas (at constant temperature) is proportional to the pressure applied to it.
- Example: a gas in an 8 L container has a pressure of 5 atm. If the volume of the container is changed to 4 L (half the initial volume) then the pressure of the gas will double (it will become 10 atm), provided the temperature of the gas is held constant.

Temperature (T) held constant
Amount of gas (n) is constant
Pressure (P) doubles, volume (V) cut in half
Boyle’s law: a pressure-volume relationship

• There is an inverse relationship between gas pressure and volume.
  – As pressure increases, volume decreases
  – As pressure decreases, volume increases
Boyle’s law: a pressure-volume relationship

• The equation that expresses Boyle’s law is:

\[ P_1 V_1 = P_2 V_2 \]

Initial \quad Final

Equation holds as long as T (temperature) is constant

\[ P_1 = \text{pressure of the gas under the first set of conditions} \]
\[ V_1 = \text{volume of the gas under the first set of conditions} \]
\[ P_2 = \text{pressure of the gas under the second set of conditions} \]
\[ V_2 = \text{volume of the gas under the second set of conditions} \]
Boyle’s law: a pressure-volume relationship

- A sample of H₂ gas occupies a volume of 2.25 L at a pressure of 628 mm Hg and a temperature of 35°C. What volume will it occupy (L) if the pressure is decreased to 428 mm Hg while the temperature is held constant?

\[ P_1 V_1 = P_2 V_2 \]

Sets of conditions:
1) Pressure = 628 mm Hg; V = 2.25 L
2) Pressure = 428 mm Hg, V = ?

\[
(628 \text{ mm}_\text{Hg})(2.25 \text{L}) = (428 \text{mm}_\text{Hg}) V_2 \\
\frac{(628 \text{mm}_\text{Hg})(2.25 \text{L})}{(428 \text{mm}_\text{Hg})} = V_2 \\
V_2 = 3.30 \text{L}
\]
Boyle’s law: a pressure-volume relationship

Same problem with different units of pressure

- A sample of $\text{H}_2$ gas occupies a volume of 2.25 L at a pressure of 0.826 atm and a temperature of 35°C. What volume will it occupy (L) if the pressure is decreased to 0.563 atm while the temperature is held constant?

$$P_1V_1 = P_2V_2$$

Sets of conditions:
1) Pressure = 0.826 mm Hg; $V = 2.25$ L
2) Pressure = 0.563 mm Hg, $V = ?$

$$\left(\frac{0.826 \text{ atm}}{0.563 \text{ atm}}\right)\left(\frac{2.25 L}{2.25 L}\right) = V_2$$

$$V_2 = 3.30L$$

Notice: units of pressure don’t matter in this equation.
Charles’s law: a temperature-volume relationship

• Charles’s law tells us that the volume of a fixed amount of gas is proportional to the absolute (Kelvin) temperature of the gas, provided the pressure of the gas is held constant (and no change in mol of gas):

\[
\frac{V_1}{T_1} = \frac{V_2}{T_2}
\]

• \(V_1\) = volume of gas in first set of conditions
• \(T_1\) = temperature of gas (in K), first set of conditions
• \(V_2\) = volume of gas, second set of conditions
• \(T_2\) = temperature of gas (in K), second set of conditions

Charles’s Law expresses a direct relationship between temperature (K) and gas volume.
Charles’s law: a temperature-volume relationship

• A sample of dry air with a volume of 125 mL at a temperature of 53°C is heated at a constant pressure to 95°C. What is the new volume (mL) of the sample?

Conditions:
1) Volume = 125 mL; temperature = 53°C (= 326K)
2) Volume = ?; temperature = 95°C (= 368K)

\[ \frac{V_1}{T_1} = \frac{V_2}{T_2} \]
\[ \frac{125 mL}{326 K} = \frac{V_2}{368 K} \]
\[ \frac{(125 mL)(368 K)}{(326 K)} = V_2 \]
\[ V_2 = 141 mL \]

Going from the first set of conditions to the second, the temperature increased. Charles’s law tells us that the volume will increase in proportion to the increase in the absolute temperature of the gas.
Combined gas law

- Boyle’s law tells us that the volume occupied by a gas is inversely proportional to the pressure of the gas (constant T and n)
- Charles’s law tells us that the volume of a gas is directly proportional to the temperature of the gas (constant P and n)
- If both pressure and temperature vary, the volume of a gas can be calculated using the combined gas law:

\[
\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}
\]
Combined gas law

- A helium-filled balloon, when released, has a volume of 10.0 L at 27\(^\circ\)C and a pressure of 663 mm Hg. What volume, in liters, will the balloon occupy at an altitude where the pressure is 96 mm Hg and the temperature -30.0\(^\circ\)C?

**Conditions:**
1) Volume = 10.0 L; temperature = 27\(^\circ\)C (= 300K); pressure = 663 mm Hg
2) Volume = ?; temperature = -30.0\(^\circ\)C (= 243K); pressure = 96 mm Hg

\[
\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}
\]

\[
\frac{(663\text{ mm}_\text{ Hg})(10.0\text{L})}{(300\text{K})} = \frac{(96\text{ mm}_\text{ Hg})V_2}{(243\text{K})}
\]

\[
\frac{(663\text{ mm}_\text{ Hg})(10.0\text{L})}{(300\text{K})} = \frac{(243\text{K})}{(96\text{ mm}_\text{ Hg})} = V_2
\]

56L = V_2
Gas Laws

- If a problem is encountered that consists of two sets of conditions ("initial" and "final") then one of the following laws is used to solve the problem:

$$P_1V_1 = P_2V_2 \quad \text{Boyle's Law}$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \text{Charles's Law}$$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \text{Combined gas law}$$
The ideal gas equation

- The ideal gas equation describes the relationships between pressure, volume, temperature, and amount of gas (moles).

\[ PV = nRT \]

- A constant, \( R \), permits conversion of units. Its value depends on the units of pressure and volume used:

\[ R = 0.0821 \frac{Latm}{mol \cdot K} \]

\[ R = 62.4 \frac{Ltorr}{mol \cdot K} \]
The ideal gas equation

- Calculate the volume (L) occupied by 3.25 moles of Cl\(_2\)(g) at 1.54 atm pressure and a temperature of 213\(^\circ\)C.

\[ PV = nRT \]

\[ V = \frac{nRT}{P} \]

\[ V = \frac{(3.25 \text{ mol}) \left(0.0821 \frac{L \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(486K)}{(1.54 \text{ atm})} \]

\[ V = 84.2L \]
The ideal gas equation

Sample problem

• Determine the pressure of 0.500 mol of $N_2(g)$ (in atm) at $35^\circ$C in a 1.00 L container.

\[
PV = nRT
\]

\[
P = ?
\]

\[
V = ?
\]

\[
n = ?
\]

\[
T = ?
\]
The ideal gas equation

Sample problem

• Determine the mass (in grams) of $N_2(g)$ in a 5.00 L container that has a pressure of 650 mm Hg at temperature of 50.0°C.
Dalton’s law of partial pressures

• Gas pressure is created by gas molecules colliding with the container walls.

• Pressure of a gas is directly proportional to the number of gas molecules.

\[ P \propto n \]

As \( n \) increases, \( P \) increases

Assume constant temperature and volume here
Initially:

Pressure = 2 atm

After addition:

Double the amount of gas (at constant volume, temp), pressure doubles

Pressure = 4 atm
Does it matter if the second gas is the same kind as the first? No.

initially      after addition

container

Pressure = 2 atm   Pressure = 4 atm

double the amount of gas

Total pressure is only affected by the total number of gas molecules, not their identities.

Assume constant temperature and volume
Dalton’s law of partial pressures

Mixtures of gases and gas pressure

• It doesn’t matter what kind of gas molecule creates this pressure.

• Thus, in a mixture of gases, the total pressure exerted by the gas mixture is the sum of the pressures exerted by each of the gases in the mixture.

\[ P_{\text{total}} = P_A + P_B + P_C + \ldots \]
Dalton’s law of partial pressures

• The pressures exerted by each gas in the mixture are called partial pressures.

• The *partial pressure* of a gas is the pressure that would be exerted by a gas in a mixture of gases if it were present alone under the same conditions.
Dalton’s law of partial pressures

• In this coming week’s lab, you’ll collect \( \text{H}_2(\text{g}) \) over water (makes it easier to determine the volume of gas).

• Water evaporates at temperatures above \( 0^\circ \text{C} \). Thus, in the experiment, the pressure of the gas you’ll collect will partially be due to \( \text{H}_2(\text{g}) \), and partially due to \( \text{H}_2\text{O}(\text{g}) \)

\[
\text{P}_{\text{total}} = \text{P}_{\text{H}_2} + \text{P}_{\text{H}_2\text{O}}
\]
• React HCl with Mg. Generate H$_2$(g).
• Want to determine how many moles H$_2$ produced, n

You will obtain the total pressure of the gases. Looking up the water vapor pressure, you can determine the pressure of H$_2$ alone.

Gas in this space is H$_2$(g) and H$_2$O$_{(g)}$

PV = nRT

• determine gas volume, V
• determine temperature (K)
• determine pressure of H$_2$...

Changes of state

Endothermic: heat is absorbed by a substance (or reaction) as some process happens. Exothermic: heat is released by a substance (or reaction) as some process occurs.
Evaporation of liquids

- **Evaporation** is the process by which molecules escape from the **liquid state into the gas state**
- Evaporation happens **at the interface** of a liquid and a gas (i.e. at the surface) – there are fewer attractions to other liquid molecules at the surface
Evaporation of liquids

• Evaporation cools a body because it’s an endothermic process ($\text{H}_2\text{O}$ absorbs heat)

• As the most energetic molecules of the liquid (the ones at the highest temperature) exit to the gas phase, the temperature of the liquid drops.
Vapor pressure of liquids

- A glass of water left on a countertop overnight will slowly evaporate. We know this because the level of the water in the glass drops with time.

- In a closed container, evaporation still happens, but the gas molecules formed cannot leave the container. They can be re-captured by the liquid phase and brought back into that phase (condensation).

Equilibrium: a condition in which two opposed processes have the same rate.
Vapor pressure of liquids

- The pressure exerted by a vapor in equilibrium with a liquid in a closed container is constant and is called the vapor pressure.
- Vapor pressure is influenced by temperature and also by the nature of the liquid.
- Some liquids consist of molecules that have very weak attractive forces between them. These liquids evaporate easily. They have high vapor pressures (called volatile).
Vapor pressure of liquids

Vapor pressure of water as a function of temperature.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Vapor Pressure (mm Hg)</th>
<th>Temperature (°C)</th>
<th>Vapor Pressure (mm Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.6</td>
<td>50</td>
<td>92.5</td>
</tr>
<tr>
<td>10</td>
<td>9.2</td>
<td>60</td>
<td>149.4</td>
</tr>
<tr>
<td>20</td>
<td>17.5</td>
<td>70</td>
<td>233.7</td>
</tr>
<tr>
<td>25&lt;sup&gt;a&lt;/sup&gt;</td>
<td>23.8</td>
<td>80</td>
<td>355.1</td>
</tr>
<tr>
<td>30</td>
<td>31.8</td>
<td>90</td>
<td>525.8</td>
</tr>
<tr>
<td>37&lt;sup&gt;b&lt;/sup&gt;</td>
<td>37.1</td>
<td>100</td>
<td>760.0</td>
</tr>
<tr>
<td>40</td>
<td>55.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Room temperature
<sup>b</sup>Body temperature

Important points:
1. Vapor pressure increases with increasing temperature.
2. The vapor pressure of H₂O at its boiling point is 760 mm Hg (1 atm).
Boiling and boiling point

- Evaporation tends to occur at the air-liquid interface.
- If the temperature of the liquid is made high enough, evaporation from the interior of the liquid can be made to occur (in bubbles).
- Boiling is a kind of evaporation in which the liquid-to-gas change of state occurs within the body of the liquid.
- The **boiling point** is the **temperature** at which the liquid’s vapor pressure equals the external pressure.
Boiling and boiling point

• The factor that has the greatest influence on a liquid’s boiling point is the external pressure (e.g. atmospheric pressure).
• Increasing the external pressure causes the boiling point to increase, while decreasing it will lower the boiling point.

<table>
<thead>
<tr>
<th>Location</th>
<th>Feet Above Sea Level</th>
<th>$P_{\text{atm}}$ (mm Hg)</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>top of Mt. Everest, Tibet</td>
<td>29,028</td>
<td>240</td>
<td>70</td>
</tr>
<tr>
<td>top of Mt. McKinley, Alaska</td>
<td>20,320</td>
<td>340</td>
<td>79</td>
</tr>
<tr>
<td>Leadville, Colorado</td>
<td>10,150</td>
<td>430</td>
<td>89</td>
</tr>
<tr>
<td>Salt Lake City, Utah</td>
<td>4,390</td>
<td>650</td>
<td>96</td>
</tr>
<tr>
<td>Madison, Wisconsin</td>
<td>900</td>
<td>730</td>
<td>99</td>
</tr>
<tr>
<td>New York City, New York</td>
<td>10</td>
<td>760</td>
<td>100</td>
</tr>
<tr>
<td>Death Valley, California</td>
<td>−282</td>
<td>770</td>
<td>100.4</td>
</tr>
</tbody>
</table>

More atmosphere exists above sea-level, so atmospheric pressure there is higher.

As elevation increases, boiling point decreases.
Intermolecular forces in liquids

- **Intermolecular forces** are attractive (cohesive) forces that operate between molecules. They consist of:
  1. Dipole-dipole forces
  2. Hydrogen bonding
  3. London forces
  4. Ion-dipole forces (look at these next chapter)

- **Intramolecular forces** operate within a single molecule. We already looked at one of these (covalent bonding)

- Covalent bonds are much stronger than any of the above intermolecular forces; however, intermolecular forces are strong enough to have significant influences on physical properties.
Intermolecular forces in liquids

• Intermolecular forces are cohesive forces – they hold molecules close to each other. Therefore, if the intermolecular forces in a liquid are strong, it is difficult for these molecules to evaporate.

• For these liquids, boiling points are high (and they are considered to be non-volatile).
**Intermolecular forces in liquids**

- **Dipole-dipole interactions** are intermolecular forces that result from interactions between polar molecules.
- The negative “pole” of one polar molecule interacts with the positive “pole” of a second molecule. (The resulting electrostatic attraction is the dipole-dipole interaction.)
- The more polar the molecule, the stronger are the dipole-dipole forces.

To have dipole-dipole forces, molecules must be polar.
Intermolecular forces in liquids

- **Hydrogen bonding** is a special case of dipole-dipole interaction, occurring in hydrogen-containing molecules where hydrogen is bonded to either O, N, or F (all very electronegative atoms).
- This makes for a very polar bond in which the hydrogen side is essentially a bare nucleus.
- The H-atom in such a bond can interact very strongly with the non-bonding pairs on O, N, and F-atoms of other molecules.
- **H-bonding is the strongest intermolecular force**

To exhibit H-bonding, molecules must possess H-X bonds, where X = O, N, or F.
Intermolecular forces in liquids

- H-bonding doesn’t need to occur between molecules of the same type. The H-bond just needs to involve:
  - H-atom bonded to O, N, or F
  - A non-bonding pair of electrons on a second O, N, or F-atom
Intermolecular forces in liquids

- **London forces** are the weakest type of intermolecular force.

The movement of electrons around nuclei in atoms and molecules can create a very brief (temporary) dipole.
Intermolecular forces in liquids

• These “instantaneous dipoles” can cause other molecules around them to become polar for an instant. The resulting interaction is attractive (London force).
Intermolecular forces in liquids

• London forces are stronger between larger atoms (increase with number of electrons on atoms). Thus London forces become stronger with increasing molar mass.

<table>
<thead>
<tr>
<th>Halogen</th>
<th>Molecular Weight (amu)</th>
<th>Boiling Point (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F\textsubscript{2}</td>
<td>38.0</td>
<td>85.1</td>
</tr>
<tr>
<td>Cl\textsubscript{2}</td>
<td>71.0</td>
<td>238.6</td>
</tr>
<tr>
<td>Br\textsubscript{2}</td>
<td>159.8</td>
<td>332.0</td>
</tr>
<tr>
<td>I\textsubscript{2}</td>
<td>253.8</td>
<td>457.6</td>
</tr>
</tbody>
</table>

London forces are present in all molecules
Intermolecular forces in liquids

Boiling point (°C)

Number of period (horizontal row) in periodic table of central atom (O, S, Se, Te)

H₂O (actual b.p. = 100°C)
H₂S
H₂Se
H₂Te

Group VIA
O
S
Se
Te

H₂O
(predicted b.p. = −80°C)

H₂S
(−60.3°C)

H₂Se
(−41.3°C)

H₂Te
(−2.2°C)