

Chem101: General Chemistry

Lecture 6 – States of Matter

I. Introduction

- A. Matter has three possible states:
 - 1. Solid
 - 2. Liquid
 - 3. Gas
- B. In this lecture we will investigate the differences in the physical properties exhibited by each of these states
 - 1. We will work to gain understanding of the forces and interactions between molecules that determine these states.
- C. In Chapter 4 (Section 4.11) we saw that the state of pure substances depends on the temperature.

Table 4.8 – Behavior of selected pure substances on heating.

- 1. We will also see that it depends on pressure.
- D. Interparticle forces were also discussed in Chapter 4 (Section 4.11).
 - 1. We will see that the magnitude of these forces influences the state of matter.
- E. At normal temperatures and pressures, the pure forms of most of the elements are solids.
 - 1. There are only two liquids, bromine and mercury.
 - 2. And eleven gases
 - a. The noble gases, helium(He), neon (Ne), argon(Ar), krypton(Kr), xenon(Xe), radon(Rn)
 - b. Plus a group of elements located in the upper right-hand corner of the periodic table: hydrogen(H₂), fluorine(F₂), chlorine(Cl₂), oxygen(O₂) and Nitrogen(N₂).

II. Observed Properties of Matter

- A. The states of matter can be easily distinguished from one another based on four properties:
 - 1. **Density**
 - a. Density is a characteristic property of pure substances
 - b. Solids and liquids are much more dense than gases.
 - i. The solid and liquid states of a particular pure substance have very similar densities.
 - 1. The solid is usually slightly more dense than the liquid.
 - 2. Water is an exception, which is why ice floats.
 - 2. **Shape**
 - a. Solids have well defined shapes and require no container to hold them.

- b. Liquids flow and take on the shape of their container
 - i. The volume of a container that is occupied by a liquid depends on the amount of liquid placed in the container.
- c. Gases, like liquids, flow and take on the shape of their container
 - i. Unlike liquids, gases expand to occupy the total volume of a container, regardless of the quantity of gas placed in the container.
- 3. **Compressibility** – is the ability to reduce the volume of a substance by applying pressure
 - a. Gases are highly compressible
 - b. Liquids and solids both have very low compressibilities.
- 4. **Thermal expansion** – is the increase in volume that occurs when a substance is heated.
 - a. Gases display moderately high thermal expansion
 - b. Liquids and Solids expand very little when heated.

Table 6.1 Physical properties of solids, liquids, and gases
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III. The Kinetic-Molecular Theory of Matter

- A. The kinetic-molecular theory of matter is the theory used to explain the different states of matter.
 - 1. Ancient Greeks proposed pieces of the theory over 2400 years ago.
- B. Generalizations that can be made based on this theory include:
 - 1. Matter is composed of tiny particles called **molecules**.
 - 2. The particles possess **kinetic energy** because they are in constant motion.
 - 3. The particles possess **potential energy** because they are attracted and repelled by each other.
 - 4. The average speed of a particle (kinetic energy) increases with **temperature**.
 - 5. The particles transfer energy from one to another during collisions in which no net energy is lost.
- C. The total energy of a sample of matter is equal to the sum of its kinetic and potential energies
 - 1. **Kinetic energy** (K.E.) is the energy a particle possesses because it is moving:

$$K.E. = \frac{1}{2}mv^2$$

- a. Where m is the mass of the particle, and v is its velocity.
- 2. **Potential energy** is the energy a particle possesses due to its position relative to the other particles.
 - a. The potential energy from attractive interactions increases as the particles become further apart from one another.
 - b. The potential energy from repulsive interactions increases as the particles become closer together.
 - c. Molecules can experience an array of repulsive and attractive interactions.

- i. These were discussed back in Chapter 4 (Section 4.11)

Figure 4.12 - Relative strengths of interparticle forces

3. The states of matter can be understood by considering the **cohesive** and **disruptive** influences that kinetic and potential energies have on a collection of particles:
 - a. Cohesive forces tend to hold particles together; they arise from attractive interactions (potential energy).
 - b. Disruptive forces are those that tend to separate the particles; they arise from kinetic energy and counter the effects of the cohesive forces.
 - c. Disruptive forces are directly dependent on temperature, whereas cohesive interactions are independent of temperature.
 - i. As the temperature increases the disruptive forces become greater and more dominant.

Figure 6.3 - A kinetic molecular view of solids, liquids and gases**IV. Solids**

- A. In solids the cohesive forces are much greater than the disruptive forces.
 1. In a crystalline solid, each molecule is held at a fixed location within a crystal lattice.
 2. The disruptive forces cause the molecules to vibrate at their fixed location, but does not allow the molecules to move past one another.
- B. The kinetic-molecular model of matter can explain the characteristic properties displayed by solids.
 1. *High density*
 - a. Because the cohesive forces are dominant, the molecules in a solid are very close together, which results in a greater number of molecules in a given volume.
 2. *Definite shape*
 - a. Because the molecules in a solid cannot move past one another, they maintain a defined shape.
 3. *Low compressibility*
 - a. Because the molecules in a solid are very close together, increasing the pressure is unable to move them much closer together.
 4. *Small thermal expansion*
 - a. Though heating causes the molecules in a solid to vibrate faster about their fixed positions, the cohesive force still predominates, holding them very close together.

V. Liquids

- A. In the liquid state the cohesive forces still predominate, holding the molecules almost as close together as in the solid state.
 1. The disruptive forces are strong enough, though, that the molecules do not have fixed locations, they instead are able to move about, slipping past one

another.

- B. As with solids, the kinetic-molecular model of matter can explain the characteristic properties of liquids.
1. Because the cohesive forces are able to still hold the molecules close together in liquid, their densities, compressibilities and thermal expansions are similar to their corresponding solids, because all three of these properties depend on the distances separating the molecules.
 2. Unlike solids, liquids do not have defined shapes because, unlike solids their molecules are capable of moving past one another.

VI. Gases

- A. In the gas state, the disruptive interactions predominate; the cohesive forces are no longer able to hold the molecules together.
1. In gases the molecules move about independently of one another.
 2. They come in contact with one another only when they collide.
 - a. And then only briefly before heading off in a new direction after the collision.
 - b. Between collisions the molecules travel in straight line at a constant velocity.
- B. The kinetic-molecular model of matter can explain the characteristic properties displayed by gases.
1. *Low density* – because the disruptive forces are dominant, the molecules are spread out and as far apart from one another as possible. This give gases very low densities, and therefore little mass in a giving volume
 2. *Indefinite shape* – Like liquids, the molecules can easily move past one another. They take on the shape of their container.
 3. *Large compressibility* – In gases the molecules are spread out with lots of space between them. When pressure is applied they can easily be pressed closer together.
 4. *Moderate thermal expansion* – as a gas is heated the individual molecules acquire more velocity, which means they strike the walls of the container with a greater force.

Demo - Freeze water with liquid N₂ and deflate balloon with liquid N₂

VII. Gas Laws

- A. For gases, simple mathematical equations can be derived that relate a gas's *volume, pressure and temperature*.
1. These equations are called **state equations** because they describe the state of the gas.
 2. Because the molecules in a gas do not interact strongly with one another, the identity of a gas is not important: the equations apply to all gases in the same way.
- B. The same cannot be said for liquids and solids.
1. Because the molecules in liquids and solids do interact strongly with one another, the relationship between pressure, volume and temperature are

- much more complicated and dependent on the identity of the substance.
- C. **Pressure** is defined as the force applied per unit area to a surface.
1. The pressures exerted by gases can be measured with a device called a manometer.
 2. A manometer that is used to measure atmospheric pressure is called a **barometer**.
 3. **Figure 6.5** Shows how to make a simple barometer, which was invented by Torricelli in the 1600's.

Figure 6.5 – Setting up a simple mercury barometer

4. Torricelli's barometer measures pressure by determining the height of a column of mercury that the pressure from the atmosphere can support.
 - a. Using this kind of barometer, the pressures are measured in units of millimeters of mercury (*mm-Hg*) or *Torr*, in honor of Torricelli.
 5. There is a pressure that is defined as a standard pressure.
 - a. It is the approximately equal to the average pressure exerted by the earth's atmosphere at sea level and is defined as 1 *atmosphere* (1 *atm*).
 - b. 1 *atm* is equal to 760 *Torr*.
- D. The **temperature** scale that must be used in gas law equations is the **Kelvin** scale.
1. The **Kelvin** scale has the same sized degrees as the **Celsius** scale, but it is shifted so that 0 *K* is at absolute zero.
 - a. This is the temperature at which the kinetic energy is zero.
 - i. All motion stops.
 - b. The shift is 273 °, that is 0 *K* = -273°C

VIII. Pressure, Temperature and Volume Relationships

A. Boyle's Law

Demo Stärk's Molecular Dynamics program
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1. In 1662, the Irish chemist Robert Boyle derived an equation that relates a gas's pressure to its volume when the temperature is held constant:

$$P = \frac{k}{V}$$

2. Where *k* is a constant
3. Boyle's law states that the pressure of a gas is inversely proportional to the volume of the gas.
4. A rearrangement of this equation gives:

$$PV = k$$

B. Charles's Law

1. In 1787, the French scientist Jacques Charles derived an equation that relates a gas's volume to its temperature when its pressure is held constant.

$$V = k T$$

2. Where k' is a constant.
 - a. The prime sign after the k is to distinguish this constant from the one that appeared in Boyle's law equation.
3. A rearrangement of this equation gives:

$$\frac{V}{T} = k'$$

C. Combined Gas Law

1. Boyle and Charles' Laws can be combined to give the combined gas law equation:

$$\frac{PV}{T} = k''$$

2. Initial and final states
 - a. If a gas is changed from an initial (i) to a final (f) state, then there will be a set of values for P , V , and T , for each state:
 - i. Initial state - P_i, V_i, T_i
 - ii. Final state - P_f, V_f, T_f
 - b. Applying the combined gas law to each:
 - i. Initial state: $\frac{P_i V_i}{T_i} = k''$
 - ii. Final state: $\frac{P_f V_f}{T_f} = k''$
 - c. Since both are equal to k'' , we can set them equal to each other:

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}$$

Exercise 6.25

- 6.25 A 200 mL sample of oxygen gas is collected at 26°C and a pressure of 690 Torr. What volume will the gas occupy at STP (0°C and 760 Torr)?

IX. The Ideal Gas Law

- A. The combined gas law works only if the number of gas molecules remains unchanged in going from the initial to the final states.
- B. **Avogadro's Law**
 1. Equal volumes of different gases measured at the same temperature and pressure contain equal numbers of molecules of gas.
 2. The constant in the combined gas law's equation, k'' , is directly

proportional to the number of gas molecules:

$$k'' = nk$$

- C. Combination of Boyle's, Charles's and Avogadro's Laws give the Ideal gas law equation.

$$\frac{PV}{T} = k''$$

$$\frac{PV}{T} = nk'''$$

$$\frac{PV}{T} = nR \quad (\text{Ideal Gas Law Equation})$$

$$PV = nRT$$

1. Where $R = k'''$ is the *Ideal Gas Law Constant* or *Universal Gas Constant*
 - a. $R = 0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}$
 - b. RT give the kinetic energy per mole of gas
2. An ideal gas is one that has no potential energy
 - a. It is neither attracted to the itself or to the walls of the container

X. Dalton's Law

- A. For ideal gases (no potential energy) at a fixed volume and temperature, the pressure exerted by the gas on the walls of the container is proportional to number of moles of gas present:

$$P = \frac{nRT}{V}$$

- B. Dalton's Law of partial pressures states that for a mixture of gases at a fixed volume and temperature, each gas will contribute to the total pressure in proportion to its number:

$$P_{tot} = \frac{n_A RT}{V} + \frac{n_B RT}{V} + \frac{n_C RT}{V} + \dots$$

$$P_{tot} = P_A + P_B + P_C + \dots$$

1. The contribution made by each gas is called its partial pressure
2. In lab, you made use of this relationship in the gas laws experiment when you subtracted the partial pressure of water from the total pressure to get the partial pressure of the CO_2 .

XI. Graham's Law

- A. **Effusion** is the escape of a gas through a small hole in a container.
- B. **Diffusion** is the spontaneous mixing of gases when brought together.
- C. At a fixed temperature, the average kinetic energy of all gases is the same, regardless of its identity:

$$(K.E.)_A = \frac{1}{2} m_A v_A^2$$

$$(K.E.)_B = \frac{1}{2} m_B v_B^2$$

$$(K.E.)_A = (K.E.)_B \quad (\text{when } T_A = T_B)$$

$$\frac{1}{2} m_A v_A^2 = \frac{1}{2} m_B v_B^2$$

$$m_A v_A^2 = m_B v_B^2$$

$$\frac{v_A^2}{v_B^2} = \frac{m_B}{m_A}$$

$$\left(\frac{v_A}{v_B} \right)^2 = \frac{m_B}{m_A}$$

$$\frac{v_A}{v_B} = \sqrt{\frac{m_B}{m_A}}$$

$$\frac{\text{effusion rate } A}{\text{effusion rate } B} = \sqrt{\frac{\text{molecular mass } B}{\text{molecular mass } A}} \quad (\text{Graham's Law})$$

- D. Graham's Law states that the effusion rate of a gas is inversely proportional to the square root of its molecular mass

XII. Changes in State

- A. The state of matter is consequence of the competition between potential (cohesive interactions) and kinetic energy (disruptive interactions)
1. Kinetic energy is proportional to temperature and independent of the identity of the molecules
 - a. The higher the temperature, the greater the kinetic energy, and the greater the molecule's velocity
 - i. This disrupts the cohesive (potential energy) interactions.
 2. Potential energy is not influenced by the temperature.
 - a. The contributions to the potential energy include:
 - i. Covalent bonds
 - ii. Metallic bonds
 - iii. Ionic bonds
 - iv. Hydrogen bonds
 - v. Dipole interactions
 - vi. Dispersion interactions.

- b. These are arranged in descending order of strength.
3. The stronger the cohesive energy holding the molecules together, the higher the temperature (greater the kinetic energy) required to disrupt these interactions, hence the greater the melting point and greater the boiling point.

XIII. Evaporation and Vapor Pressure

- A. Evaporation or vaporization
 1. Molecules from a liquid or solid continually escape the surface to become gas molecules.
- B. Condensation
 1. This is the opposite process where the gas molecules strike an and stick to the surface of the liquid or gas
- C. At equilibrium the rate of evaporation and condensation are equal.
 1. This occurs when a lid is placed on the container containing the liquid or gas so that the gas molecules cannot escape.

Figure 6.11 - Liquid evaporation in a closed container

- D. Vapor pressure
 1. The vapor pressure is the pressure of the vapor at equilibrium.
 2. Different liquids have different vapor pressures.
 - a. The vapor pressures depend on the strength of the cohesive intermolecular interactions which hold the molecules together in the liquid state.

Table 6.4 - Vapor pressure of various liquids at 20°C

3. The vapor pressure depends on temperature.
 - a. The higher the temperature the higher the vapor pressure.

Table 6.5 - Vapor pressure of water at various temperatures

XIV. Boiling and Boiling Point

- A. A liquid boils when its vapor pressure equals the atmospheric pressure.
 1. For example, at sea level water boils at 100°C because its vapor pressure is equal to 760 Torr (= 1 atm) at that temperature
- B. Water boils at lower temperatures at higher elevations because the atmospheric pressure drops as the elevation increases.

Table 6.6 - Variation of the boiling point of water with elevation.

- C. Increasing the pressure can be used to increase the boiling temperature of water.
 1. This is how pressure cookers work
 - a. Food cooks quicker in a pressure cooker because water boils at a higher temperature.

Table 6.7 - Boiling point of water in pressure cooker.

Pressure Above Atmospheric		Boiling Point of Water
<i>Psi</i>	<i>Torr</i>	$^{\circ}\text{C}$
5	259	108
10	517	116
15	776	121

XV. Sublimation and Melting

A. Sublimation

1. Solids also have a vapor pressure.
 - a. Molecules of the solid can escape to become gas molecules.
 - b. This process is called **sublimation**.

B. Melting point

1. Solids also convert to liquids.
 - a. This occurs when some, but not all of the interactions holding the molecules together in the solid state are disrupted by kinetic energy.
 - b. The remaining intermolecular interactions still hold the molecules next to each other, however, the molecules are able slide past one another.

C. Decomposition

1. Instead of melting, some solids will decompose when heated.
 - a. This occurs when the increasing kinetic energy breaks intramolecular (covalent) bonds, instead of non-covalent intermolecular interactions.

XVI. Energy and the States of Matter

A. Energy can be added by heating

B. When heat energy is absorbed and converted to kinetic energy, the temperature rises

1. Specific heat is the measure of how much heat is needed to increase 1 g of a substance by 1°C .

Table 6.8 - Specific heats for selected substances

C. When heat energy is absorbed and substance changes its state, the energy is converted to potential energy.

1. While the substance is changing states its temperature does not change.

Figure 6.14 - Temperature behavior of a system during changes in state