

SUBAREA I.

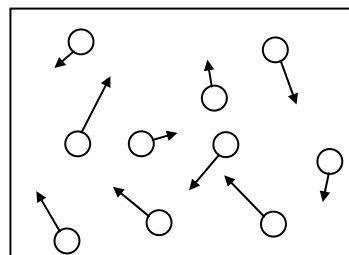
MATTER AND ENERGY; HEAT, THERMODYNAMICS, AND THERMOCHEMISTRY

COMPETENCY 1.0. MATTER AND ENERGY

Skill 1.1 Organization of matter

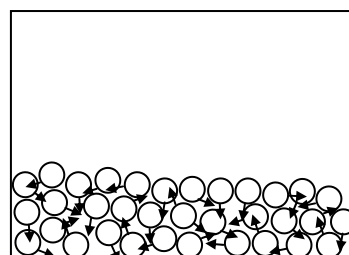
Molecules have **kinetic energy** (they move around), and they also have **intermolecular attractive forces** (they stick to each other). The relationship between these two determines whether a collection of molecules will be a gas, liquid, or solid.

A **gas** has an indefinite shape and an indefinite volume. The kinetic model for a gas is a collection of widely separated molecules, each moving in a random and free fashion, with negligible attractive or repulsive forces between them. Gases will expand to occupy a larger container so there is more space between the molecules. Gases can also be compressed to fit into a small container so the molecules are less separated.

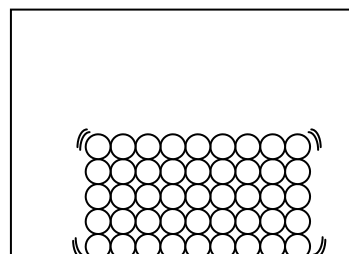


Diffusion occurs when one material spreads into or through another. Gases diffuse rapidly and move from one place to another.

A **liquid** assumes the shape of the portion of any container that it occupies and has a specific volume. The kinetic model for a liquid is a collection of molecules attracted to each other with sufficient strength to keep them close to each other but with insufficient strength to prevent them from moving around randomly. Liquids have a higher density and are much less compressible than gases because the molecules in a liquid are closer together. Diffusion occurs more slowly in liquids than in gases because the molecules in a liquid stick to each other and are not completely free to move.



A **solid** has a definite volume and definite shape. The kinetic model for a solid is a collection of molecules attracted to each other with sufficient strength to essentially lock them in place. Each molecule may vibrate, but it has an average position relative to its neighbors. If these positions form an ordered pattern, the solid is called **crystalline**. Otherwise, it is called **amorphous**. Solids have a high density and are almost incompressible because the molecules are close together. Diffusion occurs extremely slowly because the molecules almost never alter their position.



Skill 1.2 Physical and chemical properties and changes of matter

Physical changes are also known as phase changes and include condensation, melting, freezing, evaporation and sublimation. These concepts will be reviewed in Skill 2.4. Below are several important physical properties of matter.

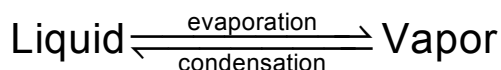
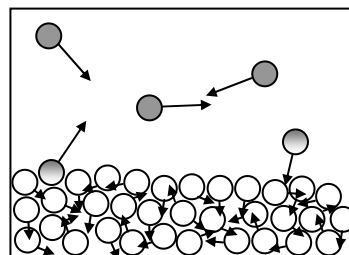
Viscosity

Viscosity measures the ability of a liquid to flow. Liquids with high viscosity flow less easily because they have strong intermolecular forces relative to kinetic energy. The viscosity of liquids decreases with temperature because it is easier for rapidly moving molecules to flow into the spaces between them. For most liquids (water is an exception), viscosity increases with pressure because the molecules are squeezed together, which forces a greater interaction, but this dependence is not as strong as the dependence on temperature.

Vapor Pressure

When a liquid is placed in a container that it does not fill entirely, there are always some molecules at the surface of the liquid (e.g., the half-shaded molecule to the left of the diagram) with enough kinetic energy to overcome the attraction of their neighbors and escape into the gas. This process is known as **evaporation**.

In a closed container, these gas molecules develop a pressure until a dynamic equilibrium occurs because the rate of their return to the liquid phase by **condensation** (e.g., the half-shaded molecule on the right in the diagram) equals the rate of their escape by evaporation:



At equilibrium, the partial pressure of the substance in the gas phase is at its **saturated vapor pressure**. Solids are also in equilibrium with vapor and have a saturated vapor pressure, though much lower due to the attraction between the molecules of a solid.

There is no real difference between the terms *gas* and *vapor*, but *gas* is often used to describe a substance that appears in the gaseous state under standard temperature and pressure and *vapor* to describe the gaseous state of a substance that appears ordinarily as a liquid or solid.

The saturated vapor pressure of a liquid is often simply called its **vapor pressure**. This term can sometimes lead to confusion when equilibrium is not present, but equilibrium is usually assumed

An increase in temperature raises vapor pressure (making the liquid more **volatile**) because kinetic energy opposes intermolecular attractions and permits more molecules to escape from the liquid phase.

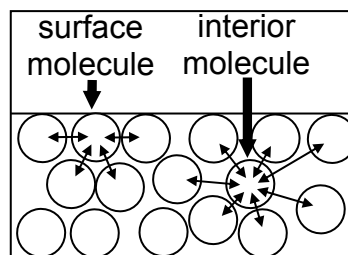
More information on vapor pressure may be found at:

<http://hyperphysics.phy-astr.gsu.edu/hbase/kinetic/vappre.html>. A flash animation of liquid/vapor equilibrium showing how vapor pressure is measured is located at:

<http://www.mhhe.com/physsci/chemistry/essentialchemistry/flash/vaporv3.swf>.

Surface Tension

The molecules on the surface of a liquid are affected by two type of intermolecular forces. One attraction is to the molecules that have evaporated and are in the air surrounding the liquid, and the other attraction is to other molecules in the liquid. The latter attraction is many times stronger than the first. So, there is a preference for the surface molecules to remain in the



liquid phase. There is a net inwards pull away from the interface between liquid and gas, which has the effect of minimizing the liquid's surface area. This is not the case for molecules in the interior of the liquid because here the forces are balanced.

Surface tension is the energy required to increase the surface area of a liquid by a unit amount. Because of surface tension, friction exists at the liquid-gas interface that makes it more difficult to move a solid object through the surface than to move it when it's completely submerged.

Temperature decreases surface tension because kinetic energy acts in opposition to intermolecular attractive forces. Chemicals with strong intermolecular attractive forces have a high surface tension. Surface tension can also be altered by adding other substances. For example, NaOH added to water will raise its surface tension and adding soap to water will lower its surface tension.

Boiling Point as a Function of Pressure

For a liquid in an open container, vapor pressure increases with temperature until it is equal to the external pressure, and the **boiling point** occurs at that temperature. Boiling is defined as the process of vapor bubbles forming and evolving from the liquid. Substances with stronger intermolecular attractive forces have a higher boiling point. An increase in the surrounding pressure forces molecules closer together and increases their intermolecular attractive forces. More kinetic energy is required to break these bonds, so **boiling point increases with pressure**.

Critical Point

In this section, we've seen how rising temperature at a gas-liquid interface increases vapor pressure and decreases surface tension. All the liquid will become a gas at the boiling point, but if the external pressure is increased above the vapor pressure, material will remain in the liquid phase and the boiling point will increase. A pressure cooker is a good example of this.

Finally, however, a temperature is reached at which no amount of pressure will keep the material in a liquid state. The highest temperature at which a substance can exist as a liquid is its **critical temperature**. **Critical pressure** is the vapor pressure of a liquid at its critical temperature. Surface tension shrinks to zero and there is no longer a gas-liquid interface when critical conditions are reached.

Above its critical temperature and pressure, a substance takes the shape and volume of its container, like a gas, but it has a density and intermolecular attractive forces similar to a liquid. This phase is called a **supercritical fluid**. Like liquids and gases, supercritical fluids are able to flow from one place to another.

Summary

The following table summarizes the properties of a liquid as temperature and pressure are altered. The speed and kinetic energy of molecules are only dependant on temperature.

Effect on a liquid of an increase in one variable with the other constant	- = decrease, 0 = no change, + = increase, NA =not applicable					
	Average speed of molecules	Average translational kinetic energy of molecules	Viscosity	Vapor pressure	Surface tension	Boiling point
Temperature	+	+	-	+	-	NA
External pressure	0	0	+/-¹	NA²	NA²	+

¹A slight increase for most materials but a slight decrease for water at some temperatures.

²Not applicable. For a pure substance in a closed container at equilibrium, external pressure forces more vapor into the liquid phase. The volume of each phase is altered but conditions at the interface remain unchanged.

Skill 1.3 Forms and transformations of matter and energy

The forms of matter are discussed in Skill 1.1. It is important to recognize that **matter is conserved** (see Skill 1.4) and so while it may undergo phase (see Skill 2.4) and chemical changes and even nuclear decay, it will never be created nor destroyed.

The **forms of energy include chemical, electrical, thermal, and mechanical**. All types of energy are important for the study of chemistry and some are discussed elsewhere in this guide (thermal energy in Competency 2.0 and electric energy in Skill 7.5). Like matter, **energy is conserved and cannot be created or destroyed** (see Skill 1.4).

Energy can be converted from one type to another. For instance, living things convert the chemical energy stored in adenosine-tri-phosphate (ATP) to mechanical energy to perform a variety of tasks.

Further, **mass and energy are related to one another via special relativity**. The total energy (E) of particle or object is related to its mass (m) via the famous equation $E = mc^2$ (where c is a constant, the speed of light in a vacuum). Note that in this equation, mass is specifically *rest mass* or mass measured independent of the observer (i.e., rest mass does not change with a change in reference). Therefore, in modern physics, all forms of energy exhibit mass and all mass is a form of energy.

Skill 1.4 Laws of conservation of mass and energy

The law of conservation of mass states that the **mass of a closed system will remain constant, regardless of the processes acting inside the system**. This means that matter can change form, but it cannot be created or destroyed. This implies that for any chemical process in a closed system, the mass of the reactants must equal the mass of the products.

Likewise, the law of conservation of energy states that **the total amount of energy in an isolated system remains constant**. The energy may be converted from one form to another, but will not be created or destroyed. Note that the conservation of energy is also the first law of thermodynamics (Skill 2.5).

COMPETENCY 2.0 HEAT AND THERMODYNAMICS

Skill 2.1 Heat and temperature; concepts; measurements and units

Energy

Energy is the **driving force for change**. Energy has units of joules (J). Temperature remains constant during phase changes, so the **speed** of molecules and their **translational kinetic energy do not change** during a change in phase.

The **internal energy** of a material is the **sum of the total kinetic energy** of its molecules and the **potential energy** of interactions between those molecules. Total kinetic energy includes the contributions from translational motion and other components of motion such as rotation. The potential energy includes **energy stored in the form of resisting intermolecular attractions** between molecules.

The **enthalpy** (H) of a material is the **sum of its internal energy and the mechanical work** it can do by driving a piston. We usually don't deal with mechanical work in high school chemistry, so the differences between internal energy and enthalpy are not important. The key concept is that a change in the **enthalpy** of a substance is the total **energy** change caused by **adding or removing heat** at constant pressure.

When a material is heated and experiences a phase change, **thermal energy is used to break the intermolecular bonds** holding the material together. Similarly, bonds are formed with the release of thermal energy when a material changes its phase during cooling. Therefore, **the energy of a material increases during a phase change that requires heat and decreases during a phase change that releases heat**. For example, the energy of H_2O increases when ice melts and decreases when water freezes.

Entropy

Entropy may be thought of as **the disorder in a system** or as a measure of the **number of states a system may occupy**. Changes due to entropy occur in one direction with no driving force. For example, a small volume of gas released into a large container will expand to fill it, but the gas in a large container never spontaneously collects itself into a small volume. This occurs because a large volume of gas has more disorder and has more places for gas molecules to be. This change occurs because **processes increase in entropy** when given the opportunity to do so.

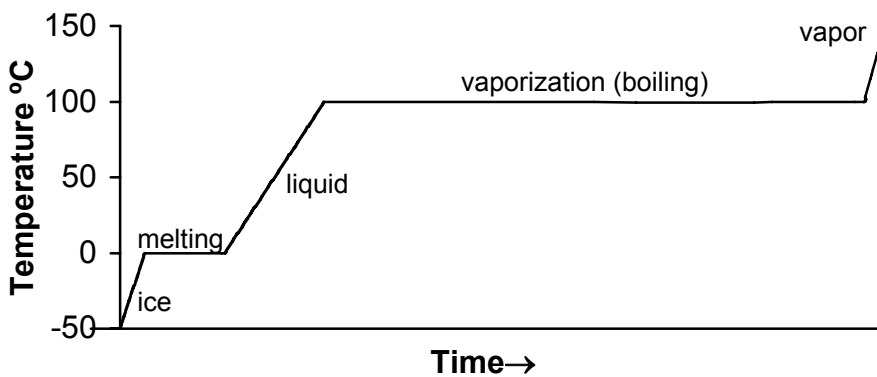
A brief definition will not help you master these concepts. But it is important that you can utilize them sufficiently to apply them to phase changes and to chemical reactions. Entropy has units of Joules/Kelvin.

Also see Skill 14.1 for more information on units and temperature scales.

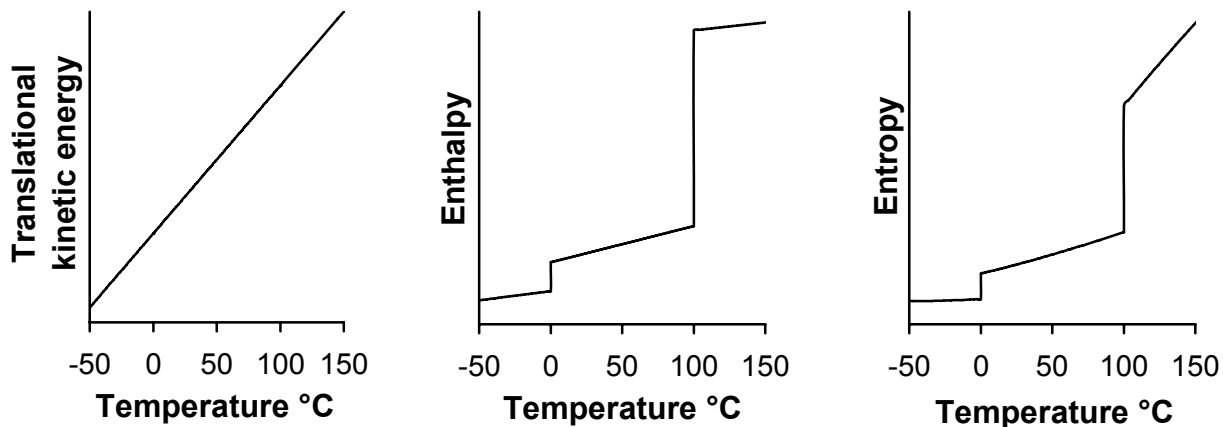
Skill 2.2 Measurement and transfer of thermal energy and its effects on matter

In the solid phase, each molecule may vibrate a little, but it is otherwise locked in place in an ordered position and may only be in a relatively small number of locations. In the gas phase, however, each molecule could be almost anywhere and there is greater disorder. Therefore, **the entropy of a material increases during a phase change that raises the freedom of molecular motion and decreases during a phase change that prevents molecular motion.** Entropy also increases with temperature because molecules experience more disorder when they have a wider range of energy states to occupy.

Raw phase change data is often charted by recording the temperature over time when heat is added at a constant rate. A diagram for water at 1 atm from -50°C to 150°C is shown below. Note that temperature does not change during melting and boiling. Also note the difference in the length of time required for melting compared to boiling. This is a result of greater energy requirements to boil a substance than to melt it.



The relationship of the translational kinetic energy, enthalpy, and entropy of water to temperature is charted below under the same conditions.



Skill 2.3 Kinetic molecular theory and gas laws

In a solid, the energy of intermolecular attractive forces is much stronger than the kinetic energy of the molecules. As temperature increases in a solid, the vibrations of individual molecules grow more intense and the molecules spread slightly further apart, decreasing the density of the solid.

In a liquid, the energy of intermolecular attractive forces is about as strong as the kinetic energy of the molecules and both play a role in the properties of liquids.

In a gas, the energy of intermolecular forces is much weaker than the kinetic energy of the molecules. Kinetic molecular theory is most commonly used to understand gases and is best applied by imagining ourselves shrinking down to become a molecule and picturing what happens when we bump into other molecules and into container walls.

Gas **pressure** results from molecular collisions with container walls. The **number of molecules** striking an **area** on the walls and the **average kinetic energy** per molecule are the only factors that contribute to pressure. A higher **temperature** increases speed and kinetic energy. There are more collisions at higher temperatures, but the average distance between molecules does not change, and thus density does not change in a sealed container.

Kinetic molecular theory explains how pressure and temperature influences behavior of gases the way they do by making a few assumptions, namely:

- 1) The energies of intermolecular attractive and repulsive forces may be neglected.
- 2) The average kinetic energy of the molecules is proportional to absolute temperature.
- 3) Energy can be transferred between molecules during collisions and the collisions are elastic, so the average kinetic energy of the molecules doesn't change due to collisions.
- 4) The volume of all molecules in a gas is negligible compared to the total volume of the container.

Strictly speaking, molecules also manifest some kinetic energy by rotating or experiencing other motions. The motion of a molecule from one place to another is called **translation**. Translational kinetic energy is the form that is transferred by collisions, and kinetic molecular theory ignores other forms of kinetic energy because they are not proportional to temperature.

The following table summarizes the application of kinetic molecular theory to an increase in container volume, number of molecules, and temperature:

Effect of an increase in one variable with other two constant	Impact on gas: - = decrease, 0 = no change, + = increase						
	Average distance between molecules	Density in a sealed container	Average speed of molecules	Average translational kinetic energy of molecules	Collisions with container walls per second	Collisions per unit area of wall per second	Pressure (P)
Volume of container (V)	+	-	0	0	-	-	-
Number of molecules	-	+	0	0	+	+	+
Temperature (T)	0	0	+	+	+	+	+

Additional details on the kinetic molecular theory may be found at <http://hyperphysics.phy-astr.gsu.edu/hbase/kinetic/ktcon.html>. An animation of gas particles colliding is located at http://comp.uark.edu/~jgeabana/mol_dyn/.

Charles's law states that the volume of a fixed amount of gas at constant pressure is directly proportional to absolute temperature, or:

$$V \propto T.$$

Boyle's law states that the volume of a fixed amount of gas at constant temperature is inversely proportional to the gas pressure, or:

$$V \propto \frac{1}{P}.$$

Gay-Lussac's law states that the pressure of a fixed amount of gas in a fixed volume is proportional to absolute temperature, or:

$$P \propto T.$$

The **combined gas law** uses the above laws to determine a proportionality expression that is used for a constant quantity of gas:

$$V \propto \frac{T}{P}.$$

The combined gas law is often expressed as an equality between identical amounts of an ideal gas at two different states ($n_1=n_2$):

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}.$$

Avogadro's hypothesis states that equal volumes of different gases at the same temperature and pressure contain equal numbers of molecules.

Avogadro's law states that the volume of a gas at constant temperature and pressure is directly proportional to the quantity of gas, or:

$$V \propto n \text{ where } n \text{ is the number of moles of gas.}$$

Avogadro's law and the combined gas law yield $V \propto \frac{nT}{P}$. The proportionality constant R --the **ideal gas constant**--is used to express this proportionality as the **ideal gas law**:

$$PV = nRT .$$

The ideal gas law ($PV = nRT$) is useful because it contains all the information of Charles's, Avogadro's, Boyle's, and the combined gas laws in a single expression.

For mixtures of gases in a container, each gas exerts a **partial pressure** that it would have if it were present in the container alone. **Dalton's law** of partial pressures states that the total pressure of a gas mixture is simply the sum of these partial pressures:

$$P_{total} = P_1 + P_2 + P_3 + \dots$$

Dalton's law may be applied to the ideal gas law:

$$P_{total}V = (P_1 + P_2 + P_3 + \dots)V = (n_1 + n_2 + n_3 + \dots)RT .$$

Effusion occurs when gas escapes through a tiny opening into a vacuum or into a region at lower pressure. **Graham's law** states that the rate of effusion (r) for a gas is inversely proportional to the square root of its molecular weight (M).

$$r \propto \frac{1}{\sqrt{M}}$$

Graham's law may be used to compare the ratios of effusion rates and molecular weights for two different gases.

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

Graham's law uses the same two expressions above to describe the dependence of the **diffusion** rate on molecular weight.