

12.6: Phase Changes

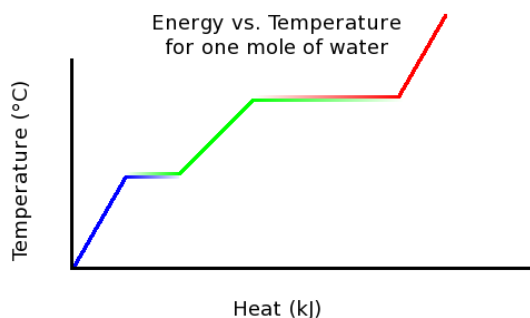
learning objectives

- Describe behavior of the medium during a phase transition

A phase of a thermodynamic system and the states of matter have uniform physical properties. During a phase transition of a given medium certain properties of the medium change, often discontinuously, as a result of some external condition, such as temperature or pressure. For example, a liquid may become gas upon heating to the boiling point, resulting in an abrupt change in volume. The measurement of the external conditions at which the transformation occurs is termed the phase transition. The term is most commonly used to describe transitions between solid, liquid and gaseous states of matter and, in rare cases, plasma.

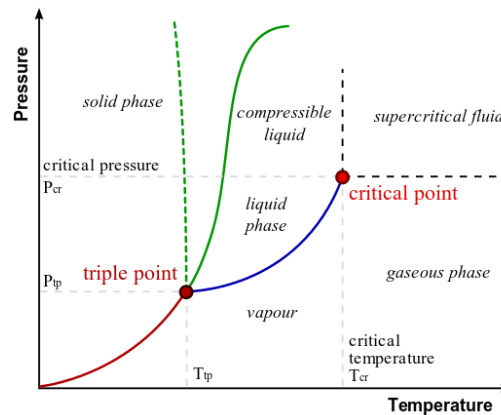
As an example, if you boil water, it never goes above 100 degrees Celsius. Only after it has completely evaporated will it get any hotter. This is because once water reaches the boiling point, extra energy is used to change the state of matter and increase the potential energy instead of the kinetic energy. The opposite happens when water freezes. To boil or melt one mole of a substance, a certain amount of energy is required. These amounts of energy are the molar heat of vaporization and molar heat of fusion. If that amount of energy is added to a mole of that substance at boiling or freezing point, all of it will melt or boil, but the temperature won't change.

Temperature increases linearly with heat, until the melting point. But the heat added does not change the temperature; that heat energy is instead used to break intermolecular bonds and convert ice into water. At this point, there is a mixture of both ice and water. Once all ice has been melted, the temperature again rises linearly with heat added. At the boiling point, temperature no longer rises with heat added because the energy is once again being used to break intermolecular bonds. Once all water has been boiled to steam, the temperature will continue to rise linearly as heat is added.



Temperature vs. Heat: This graph shows the temperature of ice as heat is added.

The plots of pressure versus temperatures provide considerable insight into thermal properties of substances. There are well-defined regions on these graphs that correspond to various phases of matter, so PT graphs are called phase diagrams. Using the graph, if you know the pressure and temperature you can determine the phase of water. The solid lines—boundaries between phases—indicate temperatures and pressures at which the phases coexist (that is, they exist together in ratios, depending on pressure and temperature). For example, the boiling point of water is 100° C at 1.00 atm. As the pressure increases, the boiling temperature rises steadily to 374° C at a pressure of 218 atm. A pressure cooker (or even a covered pot) will cook food faster because the water can exist as a liquid at temperatures greater than 100° C without all boiling away. The curve ends at a point called the critical point, because at higher temperatures the liquid phase does not exist at any pressure. The critical temperature for oxygen is -118°C, so oxygen cannot be liquefied above this temperature.



Phase Diagram of Water: In this typical phase diagram of water, the green lines mark the freezing point, and the blue line marks the boiling point, showing how they vary with pressure. The dotted line illustrates the anomalous behavior of water. Note that water changes states based on the pressure and temperature.

Humidity, Evaporation, and Boiling

The amount of water vapor in air is a result of evaporation or boiling, until an equilibrium is reached.

learning objectives

- Explain why water boils at 100 °C

Overview

The term relative humidity refers to how much water vapor is in the air compared with the maximum possible. At its maximum, denoted as saturation, the relative humidity is 100%, and evaporation is inhibited. The amount of water vapor the air can hold depends on its temperature. For example, relative humidity rises in the evening, as air temperature declines, sometimes reaching the dew point. At the dew point temperature, relative humidity is 100%, and fog may result from the condensation of water droplets if they are small enough to stay in suspension. Conversely, if one wished to dry something, it is more effective to blow hot air over it rather than cold air, because, among other things, hot air can hold more water vapor.

Evaporation

The capacity of air to hold water vapor is based on vapor pressure of water. The liquid and solid phases are continuously giving off vapor because some of the molecules have high enough speeds to enter the gas phase, a process called evaporation; see (a). For the molecules to evaporate, they must be located near the surface, be moving in the proper direction, and have sufficient kinetic energy to overcome liquid-phase intermolecular forces. When only a small proportion of the molecules meet these criteria, the rate of evaporation is low. Since the kinetic energy of a molecule is proportional to its temperature, evaporation proceeds more quickly at higher temperatures.

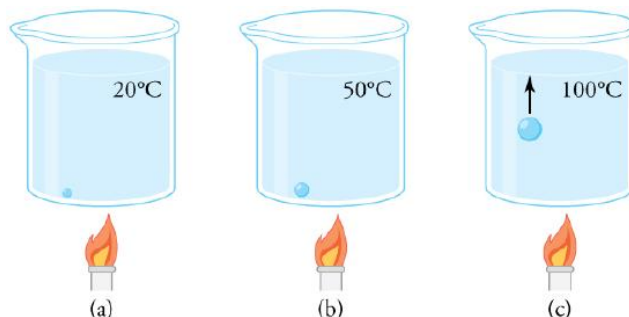
If a lid is placed over the container, as in (b), evaporation continues, increasing the pressure, until sufficient vapor has built up for condensation to balance evaporation. Then equilibrium has been achieved, and the vapor pressure is equal to the partial pressure of water in the container. Vapor pressure increases with temperature because molecular speeds are higher as temperature increases.

As the faster-moving molecules escape, the remaining molecules have lower average kinetic energy, and the temperature of the liquid decreases. This phenomenon is also called evaporative cooling. This is why evaporating sweat cools the human body. Evaporation also tends to proceed more quickly with higher flow rates between the gaseous and liquid phase and in liquids with higher vapor pressure. For example, laundry on a clothes line will dry (by evaporation) more rapidly on a windy day than on a still day.

Application for Boiling Water

Why does water boil at 100°C? The vapor pressure of water at 100°C is 1.01×10^5 Pa, or 1.00 atm. Thus, it can evaporate without limit at this temperature and pressure. But why does it form bubbles when it boils? This is because water ordinarily contains significant amounts of dissolved air and other impurities, which are observed as small bubbles of air in a glass of water. If a bubble

starts out at the bottom of the container at 20°C, it contains water vapor (about 2.30%). The pressure inside the bubble is fixed at 1.00 atm (we ignore the slight pressure exerted by the water around it). As the temperature rises, the amount of air in the bubble stays the same, but the water vapor increases; the bubble expands to keep the pressure at 1.00 atm. At 100°C, water vapor enters the bubble continuously since the partial pressure of water is equal to 1.00 atm in equilibrium. It cannot reach this pressure, however, since the bubble also contains air and total pressure is 1.00 atm. The bubble grows in size and thereby increases the buoyant force. The bubble breaks away and rises rapidly to the surface, resulting in boiling. (See.)



Close-up of the Boiling Process: (a) An air bubble in water starts out saturated with water vapor at 20°C. (b) As the temperature rises, water vapor enters the bubble because its vapor pressure increases. The bubble expands to keep its pressure at 1.00 atm. (c) At 100°C, water vapor enters the bubble continuously because water's vapor pressure exceeds its partial pressure in the bubble, which must be less than 1.00 atm. The bubble grows and rises to the surface.

Key Points

- The term is most commonly used to describe transitions between solid, liquid and gaseous states of matter and, in rare cases, plasma.
- Once water reaches the boiling point, extra energy is used to change the state of matter and increase the potential energy instead of the kinetic energy.
- Plots of pressure versus temperatures, an example of a phase diagram, provide considerable insight into thermal properties of substances.
- Relative humidity is the fraction of water vapor in a gas compared to the saturation value.
- Since the kinetic energy of a molecule is proportional to its temperature, evaporation proceeds more quickly at higher temperatures.
- Vapor pressure increases with temperature because molecular speeds are higher as temperature increases.
- Water boils at 100 °C because the vapor pressure exceeds atmospheric pressure at this temperature.

Key Terms

- **intermolecular:** from one molecule to another; between molecules
- **plasma:** a state of matter consisting of partially ionized gas
- **thermodynamic:** Relating to the conversion of heat into other forms of energy.
- **equilibrium:** The state of a body at rest or in uniform motion, the resultant of all forces on which is zero.
- **vapor pressure:** The pressure that a vapor exerts, or the partial pressure if it is mixed with other gases.
- **humidity:** The amount of water vapor in the air.

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