

4.11: Phase Transitions - Melting, Boiling, and Subliming

Learning Objective

- Describe what happens during a phase change.
- Calculate the energy change needed for a phase change.

Substances can change phase—often because of a temperature change. At low temperatures, most substances are solid; as the temperature increases, they become liquid; at higher temperatures still, they become gaseous.

The process of a solid becoming a liquid is called **melting** (an older term that you may see sometimes is *fusion*). The opposite process, a liquid becoming a solid, is called **solidification**. For any pure substance, the temperature at which melting occurs—known as the **melting point**—is a characteristic of that substance. It requires energy for a solid to melt into a liquid. Every pure substance has a certain amount of energy it needs to change from a solid to a liquid. This amount is called the **enthalpy of fusion (or heat of fusion)** of the substance, represented as ΔH_{fus} . Some ΔH_{fus} values are listed in Table 4.11.1; it is assumed that these values are for the melting point of the substance. Note that the unit of ΔH_{fus} is kilojoules per mole, so we need to know the quantity of material to know how much energy is involved. The ΔH_{fus} is always tabulated as a positive number. However, it can be used for both the melting and the solidification processes, minding that melting is always endothermic (so ΔH will be positive), while solidification is always exothermic (so ΔH will be negative).

Table 4.11.1: Enthalpies of Fusion for Various Substances

Substance (Melting Point)	ΔH_{fus} (kJ/mol)
Water (0°C)	6.01
Aluminum (660°C)	10.7
Benzene (5.5°C)	9.95
Ethanol (−114.3°C)	5.02
Mercury (−38.8°C)	2.29

✓ Example 4.11.1

What is the energy change when 45.7 g of H_2O melt at 0°C?

Solution

The ΔH_{fus} of H_2O is 6.01 kJ/mol. However, our quantity is given in units of grams, not moles, so the first step is to convert grams to moles using the molar mass of H_2O , which is 18.0 g/mol. Then we can use ΔH_{fus} as a conversion factor. Because the substance is melting, the process is endothermic, so the energy change will have a positive sign.

$$45.7 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.0 \text{ g}} \times \frac{6.01 \text{ kJ}}{\text{mol}} = 15.3 \text{ kJ}$$

Without a sign, the number is assumed to be positive.

Exercise 4.11.1

What is the energy change when 108 g of C_6H_6 freeze at 5.5°C?

Answer

−13.8 kJ

During melting, energy goes exclusively to changing the phase of a substance; it does not go into changing the temperature of a substance. Hence melting is an **isothermal** process because a substance stays at the same temperature. Only when all of a substance

is melted does additional energy go to changing its temperature.

What happens when a solid becomes a liquid? In a solid, individual particles are stuck in place because the intermolecular forces cannot be overcome by the energy of the particles. When more energy is supplied (e.g., by raising the temperature), there comes a point at which the particles have enough energy to move around, but not enough energy to separate. This is the liquid phase: particles are still in contact, but are able to move around each other. This explains why liquids can assume the shape of their containers: the particles move around and, under the influence of gravity, fill the lowest volume possible (unless the liquid is in a zero-gravity environment—see Figure 4.11.1).

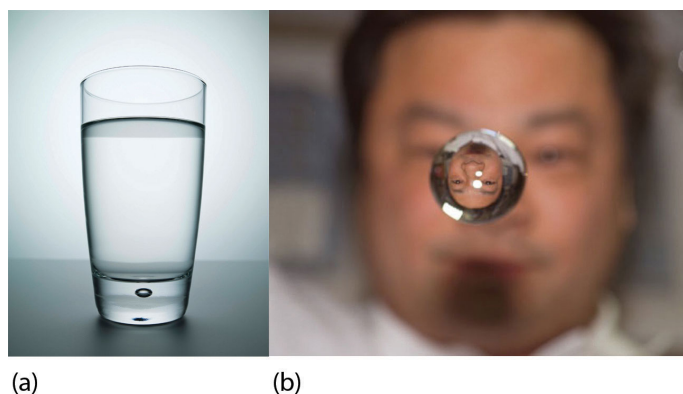


Figure 4.11.1: Liquids and Gravity. (a) A liquid fills the bottom of its container as it is drawn downward by gravity and the particles slide over each other. (b) A liquid floats in a zero-gravity environment. The particles still slide over each other because they are in the liquid phase, but now there is no gravity to pull them down. Source: Photo on the left © Thinkstock. Photo on the right courtesy of NASA, http://www.nasa.gov/mission_pages/st...image_009.html.

The phase change between a liquid and a gas has some similarities to the phase change between a solid and a liquid. At a certain temperature, the particles in a liquid have enough energy to become a gas. The process of a liquid becoming a gas is called **boiling (or vaporization)**, while the process of a gas becoming a liquid is called **condensation**. However, unlike the solid/liquid conversion process, the liquid/gas conversion process is noticeably affected by the surrounding pressure on the liquid because gases are strongly affected by pressure. This means that the temperature at which a liquid becomes a gas, the **boiling point**, can change with surrounding pressure. Therefore, we define the **normal boiling point** as the temperature at which a liquid changes to a gas when the surrounding pressure is exactly 1 atm, or 760 torr. Unless otherwise specified, it is assumed that a boiling point is for 1 atm of pressure.

Like the solid/liquid phase change, the liquid/gas phase change involves energy. The amount of energy required to convert a liquid to a gas is called the **enthalpy of vaporization** (or heat of vaporization), represented as ΔH_{vap} . Some ΔH_{vap} values are listed in Table 4.11.2; it is assumed that these values are for the normal boiling point temperature of the substance, which is also given in the table. The unit for ΔH_{vap} is also kilojoules per mole, so we need to know the quantity of material to know how much energy is involved. The ΔH_{vap} is also always tabulated as a positive number. It can be used for both the boiling and the condensation processes as long as you keep in mind that boiling is always endothermic (so ΔH will be positive), while condensation is always exothermic (so ΔH will be negative).

Table 4.11.1: Enthalpies of Vaporization for Various Substances

Substance (Normal Boiling Point)	ΔH_{vap} (kJ/mol)
Water (100°C)	40.68
Bromine (59.5°C)	15.4
Benzene (80.1°C)	30.8
Ethanol (78.3°C)	38.6
Mercury (357°C)	59.23

✓ Example 4.11.2

What is the energy change when 66.7 g of $\text{Br}_2(\text{g})$ condense to a liquid at 59.5°C ?

Solution

The ΔH_{vap} of Br_2 is 15.4 kJ/mol . Even though this is a condensation process, we can still use the numerical value of ΔH_{vap} as long as we realize that we must take energy out, so the ΔH value will be negative. To determine the magnitude of the energy change, we must first convert the amount of Br_2 to moles. Then we can use ΔH_{vap} as a conversion factor.

$$66.7 \text{ g } \cancel{\text{Br}_2} \times \frac{1 \text{ mol } \cancel{\text{Br}_2}}{159.8 \text{ g}} \times \frac{15.4 \text{ kJ}}{\cancel{\text{mol}}} = 6.43 \text{ kJ}$$

Because the process is exothermic, the actual value will be negative: $\Delta H = -6.43 \text{ kJ}$.

Exercise 4.11.2

What is the energy change when 822 g of $\text{C}_2\text{H}_5\text{OH}(\ell)$ boil at its normal boiling point of 78.3°C ?

Answer

689 kJ

As with melting, the energy in boiling goes exclusively to changing the phase of a substance; it does not go into changing the temperature of a substance. So boiling is also an isothermal process. Only when all of a substance has boiled does any additional energy go to changing its temperature.

What happens when a liquid becomes a gas? We have already established that a liquid is composed of particles in contact with each other. When a liquid becomes a gas, the particles separate from each other, with each particle going its own way in space. This is how gases tend to fill their containers. Indeed, in the gas phase most of the volume is empty space; only about 1/1,000th of the volume is actually taken up by matter (Figure 4.11.1). It is this property of gases that explains why they can be compressed, a fact that is considered in Chapter 6.

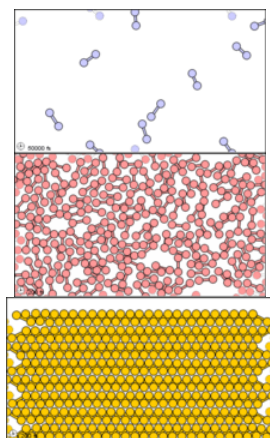


Figure 4.11.2: Sub-microscopic view of the diatomic molecules of the element bromine (a) in the gaseous state (above 58°C); (b) in liquid form (between -7.2 and 58.8°C); and (c) in solid form (below -7.2°C). As a solid, the molecules are fixed, but fluctuate. As a liquid, the molecules are in contact but are also able to move around each other. As a gas, most of the volume is actually empty space. The particles are not to scale; in reality, the dots representing the particles would be about 1/100th of the size depicted.

Under some circumstances, the solid phase can transition directly to the gas phase without going through a liquid phase, and a gas can directly become a solid. The solid-to-gas change is called **sublimation**, while the reverse process is called **deposition**. Sublimation is isothermal, like the other phase changes. There is a measurable energy change during sublimation—this energy change is called the **enthalpy of sublimation**, represented as ΔH_{sub} . The relationship between the ΔH_{sub} and the other enthalpy changes is as follows:

$$\Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}}$$

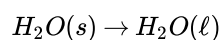
As such, ΔH_{sub} is not always tabulated because it can be simply calculated from ΔH_{fus} and ΔH_{vap} .

There are several common examples of sublimation. A well-known product, dry ice, is actually solid CO_2 . Dry ice is dry because it sublimates, with the solid bypassing the liquid phase and going straight to the gas phase. The sublimation occurs at temperature of -77°C , so it must be handled with caution. If you have ever noticed that ice cubes in a freezer tend to get smaller over time, it is because the solid water is very slowly subliming. "Freezer burn" isn't actually a burn; it occurs when certain foods, such as meats, slowly lose solid water content because of sublimation. The food is still good, but looks unappetizing. Reducing the temperature of a freezer will slow the sublimation of solid water.



Figure 4.11.3: Freezer burn on a piece of beef. (Public Domain; [RolloM.](#))

Chemical equations can be used to represent a phase change. In such cases, it is crucial to use phase labels on the substances. For example, the chemical equation for the melting of ice to make liquid water is as follows:



No chemical change is taking place; however, a physical change is taking place.

Summary

- Phase changes can occur between any two phases of matter.
- All phase changes occur with a simultaneous change in energy.
- All phase changes are isothermal.

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