

8.14: Changes of State Calculations

Learning Objectives

- Define enthalpy of fusion and enthalpy of vaporization.
- Calculate the energy changes that accompany phase changes.
- Interpret heating and cooling curves.

Everyday we take advantage of changes between the gas, liquid, and solid states to cool a drink with ice cubes (solid to liquid), cool our bodies by perspiration (liquid to gas), and cool food inside a refrigerator (gas to liquid and vice versa). We use dry ice, which is solid CO_2 , as a refrigerant (solid to gas), and we make artificial snow for skiing and snowboarding by transforming a liquid to a solid. In this section, we examine the changes in energy that occur during these changes in state or phase changes.

As introduced in an earlier section, changes of state involve changes in enthalpy ΔH , or changes in energy. Melting (changing a solid to liquid) and evaporating (changing a liquid to a gas) are both *endothermic* processes, requiring the addition of heat to break the intermolecular interactions between molecules. The reverse processes, condensation (changing a gas to a liquid) and freezing (changing a liquid to a solid), are both *exothermic*, meaning heat is given off or released when intermolecular interactions are reformed. The specific amount of energy absorbed or released when one gram of substance changes between a solid and a liquid (at the melting point) is called the **enthalpy of fusion** or heat of fusion, (ΔH_{fus}). At the boiling point, when one gram of substance changes between a liquid and a gas, the energy change is called the **enthalpy of vaporization** or heat of vaporization, (ΔH_{vap}).

Heating Curves

It is important to understand the difference between the energy associated with changes in temperature and changes in state where the temperature remains constant. This difference is most clearly depicted in a **heating curve**, which is a plot of the temperature versus heating time (or heat added). The heating curve in figure 8.14.1 is the temperature change for a 75 g sample of water as heat is added over time. The sample is initially solid (ice) at 1 atm and -23°C ; as heat is added, the *temperature* of the ice increases linearly with time. The slope of the line depends on both the mass of the ice and the specific heat (C_s) of ice, which is the amount of energy (in Joules or calories) required to raise the temperature of 1 g of ice by 1°C . As the temperature increases, the water molecules in the ice crystal absorb more and more energy and vibrate more vigorously. At the melting point, they have enough kinetic energy to overcome attractive forces and move with respect to one another. As more heat is added, the temperature of the system does *not* increase further but remains constant at 0°C until all the ice has melted. Once all the ice has been converted to liquid water, the temperature of the water again begins to increase. Now, however, the temperature increases more slowly than before because the specific heat capacity of liquid water is *greater* than that of solid water. When the temperature of the water reaches 100°C , the water begins to boil. Here, too, the temperature remains constant at 100°C until all the water has been converted to steam. At this point, the temperature again begins to rise, but at a *faster* rate than seen in the other phases because the heat capacity of steam is *less* than that of ice or water.

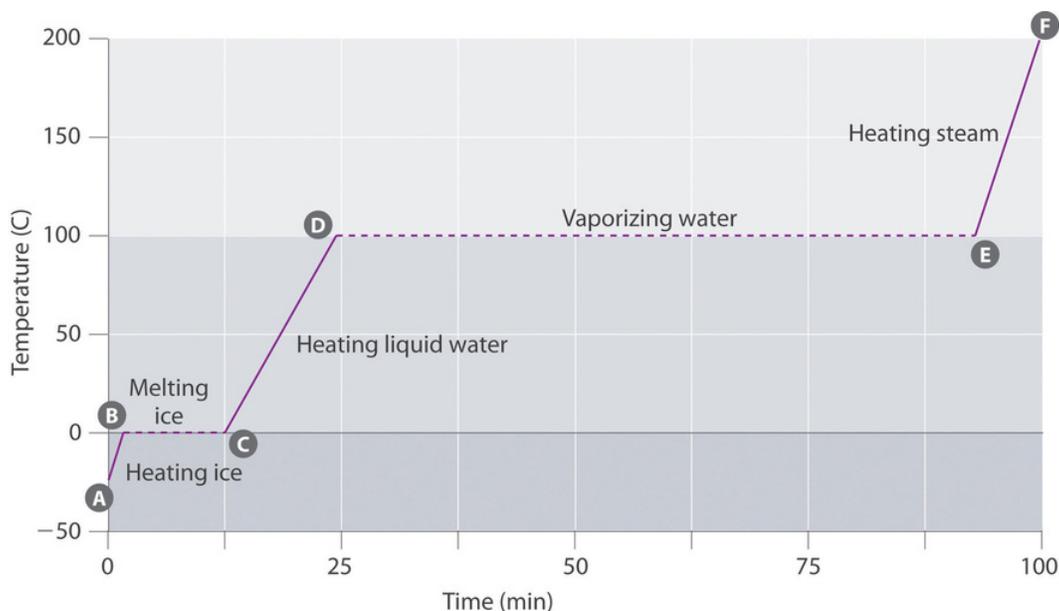


Figure 8.14.1: A Heating Curve for Water. This plot of temperature shows what happens to a 75 g sample of ice initially at 1 atm and -23°C as heat is added at a constant rate: A–B: heating solid ice; B–C: melting ice; C–D: heating liquid water; D–E: vaporizing water; E–F: heating steam.

It is worth noting again that *the temperature of a system does not change during a phase change*. In this example, as long as even a tiny amount of ice is present, the temperature of the system remains at 0°C during the melting process, and as long as even a small amount of liquid water is present, the temperature of the system remains at 100°C during the boiling process. The rate at which heat is added does *not* affect the temperature of the ice/water or water/steam mixture because the added heat is being used exclusively to overcome the attractive forces that hold the more condensed phase together. Many cooks think that food will cook faster if the heat is turned up higher so that the water boils more rapidly. Instead, the pot of water will boil to dryness sooner, but the temperature of the water does not depend on how vigorously it boils.

The temperature of a sample does not change during a phase change.

If heat is added at a constant rate, as in Figure 8.14.1, then the length of the horizontal lines, which represents the time during which the temperature does not change, is directly proportional to the magnitude of the enthalpies associated with the phase changes. In Figure 8.14.1, the horizontal line at 100°C is much longer than the line at 0°C because the enthalpy of vaporization of water is several times greater than the enthalpy of fusion.

A superheated liquid is a sample of a liquid at the temperature and pressure at which it should be a gas. Superheated liquids are not stable; the liquid will eventually boil, sometimes violently. The phenomenon of superheating causes “bumping” when a liquid is heated in the laboratory. When a test tube containing water is heated over a Bunsen burner, for example, one portion of the liquid can easily become too hot. When the superheated liquid converts to a gas, it can push or “bump” the rest of the liquid out of the test tube. Placing a stirring rod or a small piece of ceramic (a “boiling chip”) in the test tube allows bubbles of vapor to form on the surface of the object so the liquid boils instead of becoming superheated. Superheating is the reason a liquid heated in a smooth cup in a microwave oven may not boil until the cup is moved, when the motion of the cup allows bubbles to form.

Cooling Curves

The **cooling curve**, in Figure 8.14.2 plots temperature versus time as a 75 g sample of steam, initially at 1 atm and 200°C , is cooled (heat is released). Although we might expect the cooling curve to be the mirror image of the heating curve in Figure 8.14.1, the cooling curve is *not* an identical mirror image. As heat is removed from the steam, the temperature falls until it reaches 100°C . At this temperature, the steam begins to condense to liquid water. No further temperature change occurs until all the steam is converted to the liquid; then the temperature again decreases as the water is cooled. We might expect to reach another plateau at 0°C , where the water is converted to ice; in reality, however, this does not always occur. Instead, the temperature often drops below the freezing point for some time, as shown by the little dip in the cooling curve below 0°C . This region corresponds to an unstable form of the liquid, a supercooled liquid. If the liquid is allowed to stand, if cooling is continued, or if a small crystal of the solid phase is added (a seed crystal), the supercooled liquid will convert to a solid, sometimes quite suddenly. As the water freezes, the

temperature increases slightly due to the heat evolved during the freezing process and then holds constant at the melting point as the rest of the water freezes. Subsequently, the temperature of the ice decreases again as more heat is removed from the system.

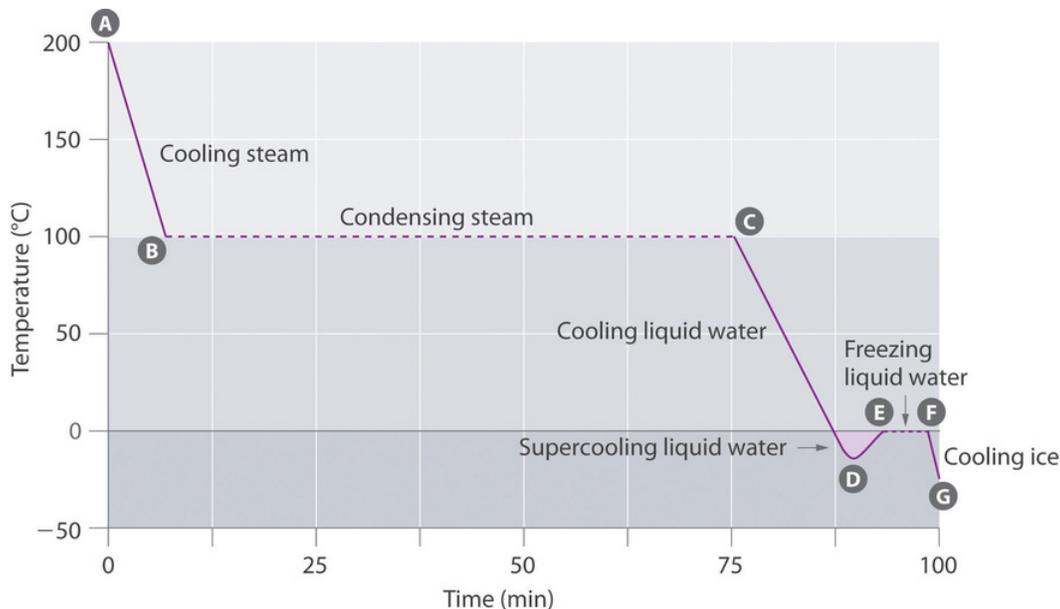


Figure 8.14.2: A Cooling Curve for Water. This plot of temperature shows what happens to a 75 g sample of steam initially at 1 atm and 200°C as heat is removed at a constant rate: A–B: cooling steam; B–C: condensing steam; C–D: cooling liquid water to give a supercooled liquid; D–E: warming the liquid as it begins to freeze; E–F: freezing liquid water; F–G: cooling ice.

Supercooling effects have a huge impact on Earth's climate. For example, supercooling of water droplets in clouds can prevent the clouds from releasing precipitation over regions that are persistently arid as a result. Clouds consist of tiny droplets of water, which in principle should be dense enough to fall as rain. In fact, however, the droplets must aggregate to reach a certain size before they can fall to the ground. Usually a small particle (a *nucleus*) is required for the droplets to aggregate; the nucleus can be a dust particle, an ice crystal, or a particle of silver iodide dispersed in a cloud during *seeding* (a method of inducing rain). Unfortunately, the small droplets of water generally remain as a supercooled liquid down to about -10°C , rather than freezing into ice crystals that are more suitable nuclei for raindrop formation. One approach to producing rainfall from an existing cloud is to cool the water droplets so that they crystallize to provide nuclei around which raindrops can grow. This is best done by dispersing small granules of solid CO_2 (dry ice) into the cloud from an airplane. Solid CO_2 sublimates directly to the gas at pressures of 1 atm or lower, and the enthalpy of sublimation is substantial (25.3 kJ/mol). As the CO_2 sublimates, it absorbs heat from the cloud, often with the desired results.



A Video Discussing the Thermodynamics of Phase Changes. Video Source: [The Thermodynamics of Phase Changes, YouTube](#)(opens in new window) [youtu.be]

✓ Example 8.14.1: Cooling Tea

If a 50.0 g ice cube at 0.0°C is added to 500 mL of tea at 20.0°C, what is the temperature of the tea when the ice cube has just melted? Assume that no heat is transferred to or from the surroundings. The density of water (and iced tea) is 1.00 g/mL over the range 0°C–20°C, the specific heats of liquid water and ice are 4.184 J/(g•°C) and 2.062 J/(g•°C), respectively, and the enthalpy of fusion of ice is 6.01 kJ/mol.

Given: mass, volume, initial temperature, density, specific heats, and ΔH_{fus}

Asked for: final temperature

Strategy

Substitute the given values into the general equation relating heat gained (by the ice) to heat lost (by the tea) to obtain the final temperature of the mixture.

Solution

When two substances or objects at different temperatures are brought into contact, heat will flow from the warmer one to the cooler. The amount of heat that flows is given by

$$q = mC_s\Delta T$$

where q is heat, m is mass, C_s is the specific heat, and ΔT is the temperature change. Eventually, the temperatures of the two substances will become equal at a value somewhere between their initial temperatures. Calculating the temperature of iced tea after adding an ice cube is slightly more complicated. The general equation relating heat gained and heat lost is still valid, but in this case we also have to take into account the amount of heat required to melt the ice cube from ice at 0.0°C to liquid water at 0.0°C.

The amount of heat gained by the ice cube as it melts is determined by its enthalpy of fusion in kJ/mol:

$$q = n\Delta H_{fus}$$

For our 50.0 g ice cube:

$$\begin{aligned} q_{ice} &= 50.0g \cdot \frac{1 \text{ mol}}{18.02 \text{ g}} \cdot 6.01 \text{ kJ/mol} \\ &= 16.7 \text{ kJ} \end{aligned}$$

Thus, when the ice cube has just melted, it has absorbed 16.7 kJ of heat from the tea. We can then substitute this value into the first equation to determine the change in temperature of the tea:

$$\begin{aligned} q_{tea} = -16,700J &= 500mL \cdot \frac{1.00g}{1mL} \cdot 4.184J/(g \cdot ^\circ C) \Delta T \\ \Delta T &= -7.98^\circ C = T_f - T_i \\ T_f &= 12.02^\circ C \end{aligned}$$

This would be the temperature of the tea when the ice cube has just finished melting; however, this leaves the melted ice still at 0.0°C. We might more practically want to know what the final temperature of the mixture of tea will be once the melted ice has come to thermal equilibrium with the tea. To determine this, we can add one more step to the calculation by plugging in to the general equation relating heat gained and heat lost again:

$$\begin{aligned} q_{ice} &= -q_{tea} \\ q_{ice} &= m_{ice}C_s\Delta T = 50.0g \cdot 4.184J/(g \cdot ^\circ C) \cdot (T_f - 0.0^\circ C) \\ &= 209.2J/^\circ C \cdot T_f \\ q_{tea} &= m_{tea}C_s\Delta T = 500g \cdot 4.184J/(g \cdot ^\circ C) \cdot (T_f - 12.02^\circ C) = 2092J/^\circ C \cdot T_f - 25,150J \\ 209.2J/^\circ C \cdot T_f &= -2092J/^\circ C \cdot T_f + 25,150J \\ 2301.2J/^\circ C \cdot T_f &= 25,150J \end{aligned}$$

$$T_f = 10.9^\circ\text{C}$$

The final temperature is in between the initial temperatures of the tea (12.02°C) and the melted ice (0.0°C), so this answer makes sense. In this example, the tea loses much more heat in melting the ice than in mixing with the cold water, showing the importance of accounting for the heat of phase changes!

? Exercise 8.14.1: Death by Freezing

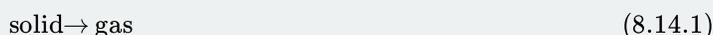
Suppose you are overtaken by a blizzard while ski touring and you take refuge in a tent. You are thirsty, but you forgot to bring liquid water. You have a choice of eating a few handfuls of snow (say 400 g) at -5.0°C immediately to quench your thirst or setting up your propane stove, melting the snow, and heating the water to body temperature before drinking it. You recall that the survival guide you leafed through at the hotel said something about not eating snow, but you cannot remember why—after all, it's just frozen water. To understand the guide's recommendation, calculate the amount of heat that your body will have to supply to bring 400 g of snow at -5.0°C to your body's internal temperature of 37°C . Use the data in Example 8.14.1

Answer

200 kJ (4.1 kJ to bring the ice from -5.0°C to 0.0°C , 133.6 kJ to melt the ice at 0.0°C , and 61.9 kJ to bring the water from 0.0°C to 37°C), which is energy that would not have been expended had you first melted the snow.

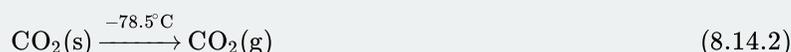
📌 Sublimation

There is also a phase change where a solid goes directly to a gas:



This phase change is called *sublimation*. Each substance has a characteristic heat of sublimation associated with this process. For example, the heat of sublimation (ΔH_{sub}) of H_2O is 620 cal/g.

We encounter sublimation in several ways. You may already be familiar with dry ice, which is simply solid carbon dioxide (CO_2). At -78.5°C (-109°F), solid carbon dioxide sublimates, changing directly from the solid phase to the gas phase:



Solid carbon dioxide is called dry ice because it does not pass through the liquid phase. Instead, it does directly to the gas phase. (Carbon dioxide *can* exist as liquid but only under high pressure.) Dry ice has many practical uses, including the long-term preservation of medical samples.

Even at temperatures below 0°C , solid H_2O will slowly sublime. For example, a thin layer of snow or frost on the ground may slowly disappear as the solid H_2O sublimates, even though the outside temperature may be below the freezing point of water. Similarly, ice cubes in a freezer may get smaller over time. Although frozen, the solid water slowly sublimates, redepositing on the colder cooling elements of the freezer, which necessitates periodic defrosting (frost-free freezers minimize this redeposition). Lowering the temperature in a freezer will reduce the need to defrost as often.

Under similar circumstances, water will also sublime from frozen foods (e.g., meats or vegetables), giving them an unattractive, mottled appearance called freezer burn. It is not really a "burn," and the food has not necessarily gone bad, although it looks unappetizing. Freezer burn can be minimized by lowering a freezer's temperature and by wrapping foods tightly so water does not have any space to sublime into.

Summary

- Phase changes are associated with energy changes.
- The enthalpy of fusion, ΔH_{fus} , is the energy absorbed or released when a substance changes between a solid and a liquid.
- The enthalpy of vaporization, ΔH_{vap} , is the energy absorbed or released when a substance changes between a liquid and a gas.
- Heating and cooling curves are useful tools to show how temperature, energy, and phases are related.

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