Pearson

11.8: Phase Diagrams

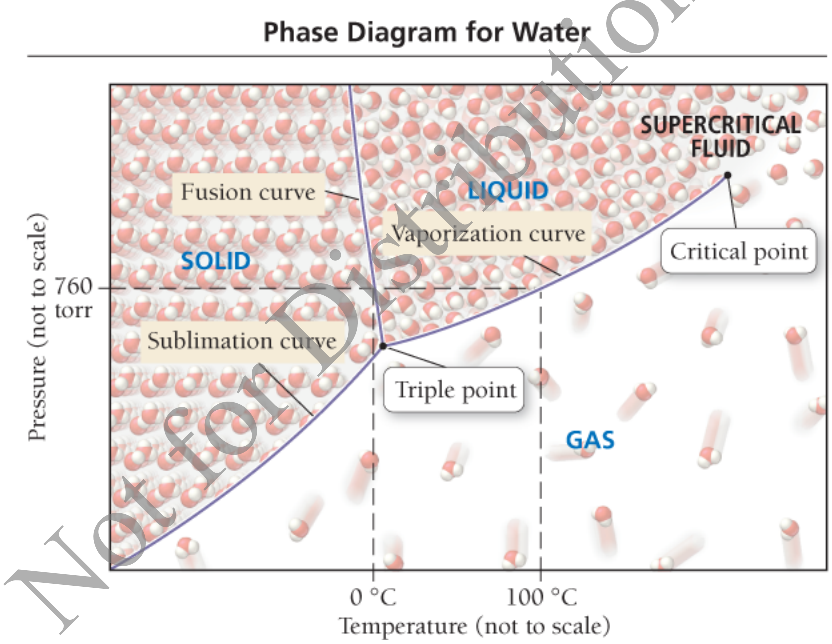
Key Concept Video **Phase Diagrams**

A **phase diagram** is a map of the state or *phase* of a substance as a function of pressure (on the *y*-axis) and temperature (on the *x*-axis). Let's first examine the major features of a phase diagram. Once we are familiar with these features, we can turn to navigating within a phase diagram, and finally examine and compare the phase diagrams of selected substances.

The Major Features of a Phase Diagram

We can become familiar with the major features of a phase diagram by examining the phase diagram for water as an example (Figure 11.34). The *y*-axis displays the pressure in torr, and the *x*-axis displays the temperature in degrees Celsius. We categorize the main features of the phase diagram as regions, lines, and points.

Figure 11.34 **Phase Diagram for Water**



Regions

Any of the three main regions—solid, liquid, and gas—in the phase diagram represents conditions where that particular state is stable. For example, under any of the temperatures and pressures within the liquid region in the phase diagram of water, the liquid is the stable state. Notice that the point 25 °C and 760 torr falls within the liquid region, as we know from everyday experience. In general, low temperature and high pressure favor the solid state, high temperature and low pressure favor the gas state, and intermediate conditions favor the liquid state. A sample of matter that is not in the state indicated by its phase diagram for a given set of conditions converts to that state when those conditions are imposed. For example, steam that is cooled to room temperature at 1 atm condenses to liquid.

Lines

Each of the lines (or curves) in the phase diagram represents a set of temperatures and pressures at which the substance is in equilibrium between the two states on either side of the line. In the phase diagram for water, consider the curved line beginning just beyond 0 °C that separates the liquid from the gas. This line is the *vaporization curve* (also called the vapor pressure curve) for water that we examined in Section 11.5. At any of the temperatures and pressures that fall along this line, the liquid and gas states of water are equally stable and in equilibrium. For example, at 100 °C and 760 torr pressure, water and its vapor are in equilibrium—they are equally stable and coexist. The other two major lines in a phase diagram are the *sublimation curve* (separating the solid and the gas) and the *fusion curve* (separating the solid and the liquid).

The Triple Point

The ***triple point*** *in a phase diagram represents the unique set of conditions at which the three states are equally stable and in equilibrium*. In the phase diagram for water, the triple point occurs at 0.0098 °C and 4.58 torr. Under these unique conditions (and only under these conditions), the solid, liquid, and gas states of water are equally stable and coexist in equilibrium.

The Critical Point

As we discussed in Section 11.5, at the critical temperature and pressure, the liquid and gas states coalesce into a *supercritical fluid*. *The* **critical point** *in a phase diagram represents the temperature and pressure above which a supercritical fluid exists*.

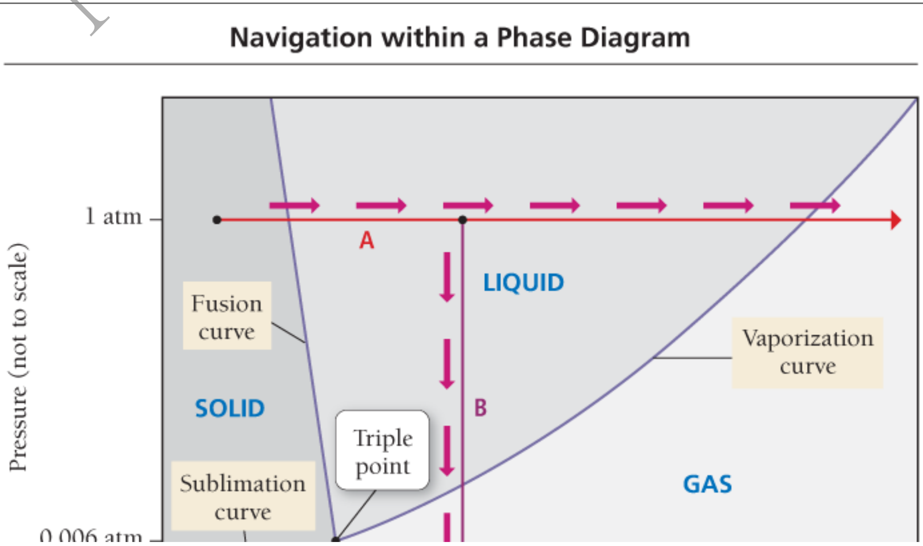
> The triple point of a substance such as water can be reproduced anywhere to calibrate a thermometer or pressure gauge with a known temperature and pressure.

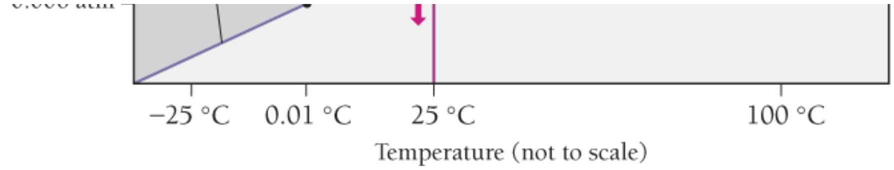
Navigation within a Phase Diagram

We represent changes in the temperature or pressure of a sample of water as movement within the phase diagram. For example, suppose we heat a block of ice initially at 1.0 atm and −25 °C. We represent the change in temperature at constant pressure as movement along the horizontal line marked A in Figure 11.35. As the temperature rises, we move to the right along the line. At the fusion curve, the temperature stops rising and melting occurs until the solid ice is completely converted to liquid water. Crossing the fusion curve requires the complete transition from solid to liquid. Once the ice has completely melted, the temperature of the liquid water begins to rise until the vaporization curve is reached. At this point, the temperature again stops rising, and boiling occurs until all the liquid is converted to gas.

We represent a change in pressure with a vertical line on the phase diagram. For example, suppose we lower the pressure above a sample of water initially at 1.0 atm and 25 °C. We represent the change in pressure at constant temperature as movement along the line marked B in Figure 11.35. As the pressure

Figure 11.35 Navigating the Phase Diagram for Water





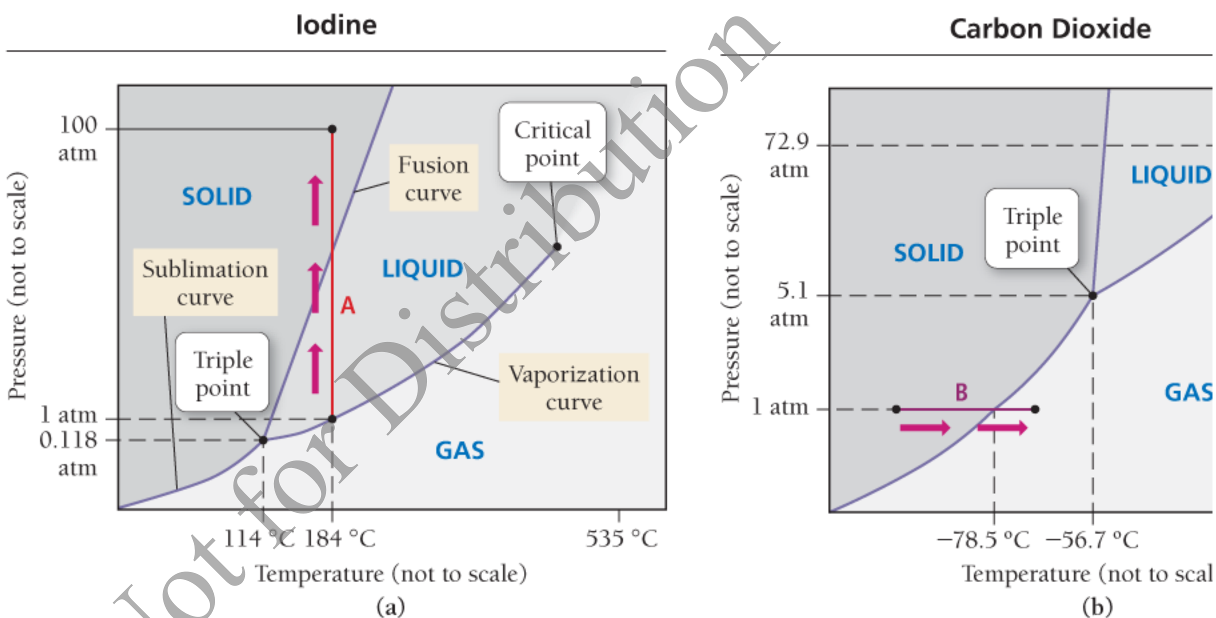
drops, we move down the line and approach the vaporization curve. At the vaporization curve, the pressure stops dropping, and vaporization occurs until the liquid is completely converted to vapor. Crossing the vaporization curve requires the complete transition from liquid to gas. Only after all the liquid has vaporized does the pressure continue to drop. Notice that, for water, the fusion curve (the line separating the solid and the liquid) slopes to the left. This means that, as the pressure increases, the liquid state is favored over the solid. This behavior is unique to water.

The Phase Diagrams of Other Substances

Examine the phase diagrams of iodine and carbon dioxide, shown in Figure 11.36. These phase diagrams are similar to that of water in most of their general features, but some significant differences exist.

Figure 11.36 Phase Diagrams for Other Substances

(**a**) Iodine and (**b**) carbon dioxide.



The fusion curves for both carbon dioxide and iodine have a positive slope—as the temperature increases, the pressure also increases—in contrast to the fusion curve for water, which has a negative slope. The behavior of water is atypical. The fusion curve within the phase diagrams for most substances has a positive slope because increasing pressure favors the denser state, which for most substances is the solid state. For example, suppose we increase the pressure on a sample of iodine from 1 atm to 100 atm at 184 °C. This change is represented by line A in Figure 11.36a. Notice that this change crosses the fusion curve, converting the liquid into a solid. In contrast, a pressure increase from 1 atm to 100 atm at –0.1 °C in water causes a state transition from solid to liquid. Unlike most substances, the liquid state of water is actually denser than the solid state.

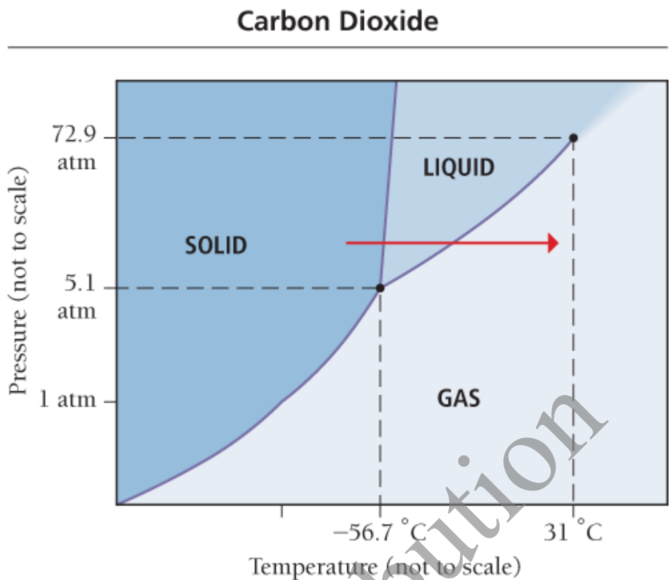
Both water and iodine have stable solid, liquid, and gaseous states at a pressure of 1 atm. Notice, however, that carbon dioxide has no stable liquid state at a pressure of 1 atm. If we increase the temperature of a block of solid carbon dioxide (dry ice) at 1 atm, as indicated by line B in Figure 11.36b, we cross the sublimation curve at –78.5 °C. At this temperature, the solid sublimes to a gas. This is one reason that dry ice is useful; it does not melt into a liquid at atmospheric pressure. Carbon dioxide forms a liquid only above pressures of 5.1 atm.

Conceptual Connection 11.7 **Phase Diagrams**

Example 11.6 Navigation within a Phase Diagram

What state transitions occur when a sample of carbon dioxide at −60.0 °C and 10.0 atm is warmed to 30.0 °C and 10.0 atm?

SOLUTION To solve this problem, draw a horizontal line on the phase diagram in Figure 11.36b beginning at −60 °C and 10.0 atm and ending at 30.0 °C and 10.0 atm.



Since the line begins in the solid region of the phase diagram, the sample is initially a solid. As the sample warms, it crosses the fusion curve and becomes a liquid. Continued warming causes it to cross the vaporization curve and become a gas. So the state transitions that occur are solid to liquid and liquid to gas.

FOR PRACTICE 11.6 Which state transitions occur in carbon dioxide if you begin with a sample of carbon dioxide at −60.0 °C at 0.50 atm and warm the sample to 30.0 °C and 0.50 atm?

Interactive Worked Example 11.6 **Navigation within a Phase Diagram**