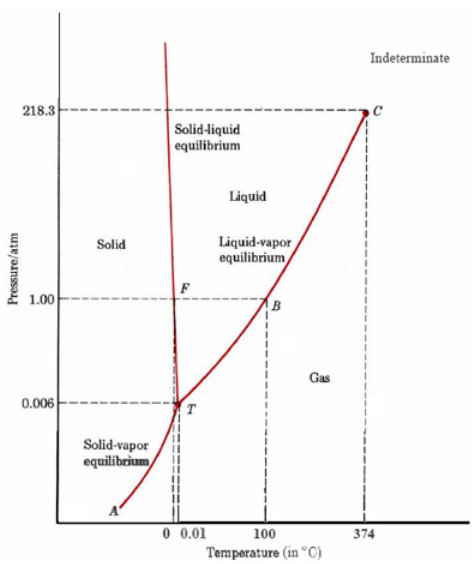
10.14: Phase Diagrams

Solids as well as liquids exhibit vapor pressure. If you hang out a wet cloth in winter, the cloth first freezes as hard as a board, but after sufficient time all the ice evaporates and the cloth becomes soft and dry. Another solid which exhibits evidence of a vapor pressure is para-dichlorobenzene, $C_6H_4Cl_2$, which is used for mothballs. The fact that you can smell this solid from across the room means that some of its molecules must have evaporated into the air and entered your nose. Indeed, given a year or so, moth crystals will evaporate completely. Still another example is dry ice, $CO_2(s)$, whose vapor pressure reaches atmospheric pressure at –78.5°C. Consequently $CO_2(s)$ sublimes, forming vapor without passing through the liquid state. Unlike ordinary ice, it remains dry, making it very convenient as a refrigerant.

Figure 10.14.1*Phase diagram of water. The scale has been distorted for purposes of diagrammatic clarity. Point T is the, triple point, C the critical point, B the boiling point, and F the freezing point.*



Like the vapor pressure of a liquid, the vapor pressure of a solid increases with temperature. This variation is usually presented in combination with other curves in a **phase diagram**, such as that for water in accompanying figure. The term *phase* in this context is used to distinguish solid, liquid, and gas, each of which has its own distinctive properties, such as density, viscosity, etc. Each phase is separated from the others by a boundary.

In the phase diagram for water, the variation of the vapor pressure of ice with temperature is shown by the line *AT*. As might be expected, the vapor pressure of ice is quite small, never rising above 0.006 atm (0.61 kPa). The vapor pressure of liquid water is usually much higher, as is shown by the curve *TC*. The point *C* on this curve corresponds to the critical point, and the vapor pressure is the critical pressure of water, 218.3 atm (22 MPa). The curve stops at this point since any distinction between liquid and gas ceases to exist above the critical temperature (this state is called a supercritical fluid).

The other end of this vapor-pressure curve, point *T*, is of particular interest. At the temperature of point *T* (273.16 K or 0.01°C) both ice and water have the same vapor pressure, 0.006 atm. Since the same vapor is in equilibrium with both liquid and solid, it follows that all three phases, ice, water, and vapor, are in equilibrium at point *T*. This point where all 3 phases exist at the same time is therefore referred to as the **triple point**.

Line *TD* remains to be discussed. This line describes how the melting point of ice varies with pressure. In other words, it includes temperatures and pressures at which solid and liquid phases are in equilibrium. Note that the line is not exactly vertical. Point *D* corresponds to a slightly lower temperature than point *T*. This means that, as we increase the pressure on ice, its freezing point decreases. Again we can draw on everyday experience for an example of this behavior. A person on a pair of skates standing on ice exerts his or her whole weight on the ice through the thin skate blade. The very high pressure immediately under the blade causes some ice to melt, affording lubrication which enables the skater to glide smoothly over the ice.

It should be emphasized that point *T* is not the normal freezing point of water. When we measure the normal freezing point of water (or any other liquid), we do so at standard atmospheric pressure in a container open to the air (part *a* of the next figure). In this container we have not only ice and water in equilibrium with each other but also *air saturated with water vapor*.

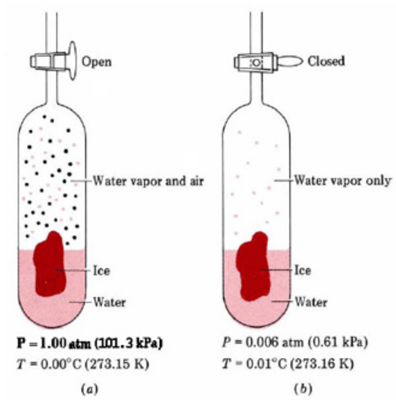


Figure 10.14.1 The normal freezing point(a) and triple point (b) of water.

The total pressure on the contents of this container is 1 atm (101.3 kPa) and its temperature is exactly 273.15 K (0.00°C). As far as liquid and solid are concerned, this corresponds to point *F* in the phase diagram.

If we could now pump all the air out of the container so that only pure water in its three phases was left, we would have the situation shown in part *b*. Ice, water, and pure water vapor, but no air, now occupy the container. The pressure has dropped from the 1.00 atm of the atmosphere to the vapor pressure (0.006 atm). Because of this decrease in pressure, the melting point of ice increases slightly and the new equilibrium temperature is 0.01°C. This corresponds to the triple point of water, point *T* in the phase diagram.

Because the triple point is more readily attained (one need not be at sea level) and also more reproducible, it is now used as a primary reference temperature for the international thermodynamic scale of temperature. In SI units the temperature of the triple point of water is defined as 273.16 K.
