Chemistry in Action Surface Melting

Freezing of water and melting of ice are phase changes that are familiar to all of us. Yet physicists and chemists have only recently begun to understand the basic aspects of these phase changes, with experimental and theoretical studies of a phenomenon known as surface melting. Experimental studies in the mid-1980s confirmed that the rigid surface arrangements of metals can become increasingly disordered several degrees below the melting point of the metal, forming a "quasiliquid layer." Many different techniques have now shown that ice also has such a fluid surface layer just a few molecules thick. This surface melting of ice might explain observations as diverse as the origin of lightning, the unique shapes of snowflakes, and ice skating.

is a loss of potential energy that was present in the liquid. At the same time energy decreases, there is a significant increase in particle order because the solid state of a substance is much more ordered than the liquid state, even at the same temperature.

Melting, the reverse of freezing, also occurs at constant temperature. As a solid melts, it continuously absorbs energy as heat, as represented by the following equation.

For pure crystalline solids, the melting point and freezing point are the same. At equilibrium, melting and freezing proceed at equal rates. The following general equilibrium equation can be used to represent these states.

At normal atmospheric pressure, the temperature of a system containing ice and liquid water will remain at 0.°C as long as both ice and water are present. That temperature will persist no matter what the surrounding temperature. Adding energy in the form of heat to such a system shifts the equilibrium to the right. That shift increases the proportion of liquid water and decreases that of ice. Only after all the ice has melted will the addition of energy increase the temperature of the system.

Molar Enthalpy of Fusion

The amount of energy as heat required to melt one mole of solid at the solid's melting point is the solid's molar enthalpy of fusion, ΔH_f . The energy absorbed increases the solid's potential energy as its particles are pulled apart, overcoming the attractive forces holding them together. At the same time, there is a significant decrease in particle order as the substance makes the transformation from solid to liquid. Similar to the molar enthalpy of vaporization, the magnitude of the molar enthalpy of fusion depends on the attraction between the solid particles.

Sublimation and Deposition

At sufficiently low temperature and pressure conditions, a liquid cannot exist. Under such conditions, a solid substance exists in equilibrium with its vapor instead of its liquid, as represented by the following equation.

The change of state from a solid directly to a gas is known as **sublimation.** The reverse process is called **deposition**, the change of state from a gas directly to a solid. Among the common substances that sublime at ordinary temperatures are dry ice (solid CO_2) and iodine. Ordinary ice sublimes slowly at temperatures lower than its melting point $(0.^{\circ}C)$. This explains how a thin layer of snow can eventually disappear, even if the temperature remains below $0.^{\circ}C$. Sublimation occurs in frost-free