MELTING AND FREEZING

Definitions

Melting – In this series of essays, melting refers to the liquification of solid ice. Melting is the process by which the solid phase of water becomes the liquid phase. The vaporization of ice (sublimation), in which solid ice becomes water vapor is not included in the melting process. That process is discussed in the essay, *Vapor, Water, and Ice* and in the essay, *Gross Vaporization*.

Freezing – Freezing is the reverse of melting. In this series of essays, freezing refers to the solidification of liquid water. In freezing, the liquid phase becomes the solid phase. The condensation of water vapor into ice is not included in the freezing process. That process is discussed in the essay, *Vapor, Water, and Ice* and in the essay, *Gross Condensation*.

The Melting Process

In an ice crystal, the intermolecular distances represent equilibrium positions between attractive and repulsive forces when the molecules are strongly aligned along the projecting axes of their constituent hydrogen atoms. This alignment is what makes ice less dense than liquid water.

This alignment of ice molecules is due to the attraction of the hydrogen ion (proton) in one molecule to one of the electron pairs in a neighboring molecule— and *vice versa*. This attraction is called the hydrogen bond, and is weaker than the bond between the hydrogen atom and the oxygen atom (covalent bond). Nevertheless, it is quite strong—strong enough that hydrogen ions frequently "jump ship" and leave one oxygen atom for a neighboring one.

In ice, a touch under two thirds of the total enthalpy is devoted to maintaining these intermolecular bonds.

THE KINETIC ATMOSPHERE
Melting and Freezing

In the free atmosphere (as opposed to the controlled conditions of the laboratory), ice in its many forms is never pure. It always contains impurities of various sorts. There will be gases, liquids, and other solids in solution. In addition, the crystalline structure is never perfect. Natural ice contains fractures, cleavages, bubbles, and other discontinuities. It contains icing nuclei and suspended solids. This means that we cannot treat it as a simple crystalline solid.

The enormous number of water molecules in even a small portion of atmospheric ice (a snowflake, for instance, or a hailstone, or a frost needle) combined with the distribution functions for the various modes of kinetic energy means that some number—no matter how small—of molecules will possess sufficient kinetic energy to break the hydrogen bonds that make up the rigid structure of an ice crystal.

Most of the thermal energy will be made manifest as kinetic energy of vibration, with the molecules moving toward and away from one another rhythmically along these axes. In addition, many of the ice molecules will have *intra*molecular energies of vibration, with the constituent atoms altering their mutual orientations in a rhythmic fashion.

In ice, just about a third of the total enthalpy is manifest in these kinetic energies of the molecules.

The breaking of the rigid intermolecular bonds occurs at any and all atmospheric temperatures—no matter how low. The distribution function, of course, is temperature dependent, with the number of molecules having such energy increasing as the temperature increases. At the melting point of ice, all added heat goes into breaking the bonds, and none of it goes into increasing the temperature.

At any given temperature, the number of ice molecules having this critical energy will stay roughly the same; but the individual molecules that make up this small population will vary from one instant to another and from one part of the ice mass to another. The mathematics of probability tells us that this population does exist, however.

Experiment also attests to the hypothesis. A drop of water-based ink placed on an ice cube will diffuse throughout the ice over time. The rate of diffusion is, of

course, temperature dependent. The colder the ice, the slower is the rate of diffusion.

As the temperature of ice increases, more and more molecules are able to break (momentarily) their bonds and move about for a short time and a short distance before realigning once again. Places in the ice where the bonding is weakest become favored sites. Impurities and discontinuities often lead to early melting.

In snowflakes, ice needles and other forms of ice with large surface areas per unit mass, the melting usually starts at the points of the crystals, where the number of molecular neighbors is fewest. Edges are the next to go, with the flats going last. Obviously, melting also starts at the outside of any ice mass and works inward, usually working along cleavages and other discontinuities.

Generally speaking, then, the melting of ice in the free atmosphere requires both an initiating event (the rise in ambient temperature or the addition of heat through radiation or conduction) and an initiating element (the weak bonding sites).

As the ice melts, its temperature remains at the melting point. The temperature of the melt water will also remain at the melting point until all of the ice is melted. Only then will the water start to warm. In the free atmosphere, ice will not be found at temperatures above 273.16°K (0.01°C).

A final note of caution: Popular belief has it that the winter snows melt in the spring to form runoff. Although this certainly and obviously happens, a considerable amount of the snow and ice simply vaporizes (sublimation). As long as the temperature of the snow and ice remains below the melting point, this is the only form of ablation that occurs.

Freezing

The Freezing Point – There is no single freezing point of atmospheric water. The freezing point of atmospheric water is somewhat dependent upon the ambient pressure, although scholars do not agree exactly how or why. In addition, it is strongly dependent upon the nature and abundance of solutes and the presence and abundance of icing nuclei. In the free atmosphere, liquid water is found at temperatures all the way down to roughly 231 K (-42°C). It is generally stable at

these supercooled temperatures, with droplets undergoing collisions, coalescence, fragmentation, strong winds, and vigorous mixing without freezing.

On the other hand, ice has been observed to form on organic proteins inside plant tissues (away from the free atmosphere) with extremely strong icing nuclei propensities at temperature up to 277 K (4°C). Under pressure (greater than atmospheric pressures), it can form stable clathrates at temperatures up to 291 K (18°C). These clathrates are essentially ice crystals surrounding molecules of some substance such as methane, propane, butane, and the like. Unless treated in some fashion, such ice can and does clog pipelines and processing equipment at these elevated temperatures.

One may thus say, with some reservations, that the melting point of atmospheric ice is 273.16 K (0.01°C). One cannot say that this is the freezing point of atmospheric water. To do so is to fly in the face of both observation and experiment.

Icing Nuclei – For some time now, we have known that exotic icing nuclei are necessary to initiate the freezing of ice. Exotic here means apart from the water molecule itself.

There are an enormous number of different aerosols that have been shown to be able to act as icing nuclei (IN). These range from ordinary dust particles to complex organic particulates, and even to living bacteria. Bacteria (both living and dead) are believed to play a very significant role in the initiation of snowflakes.

The concentration of such nuclei in the troposphere ranges from less than a hundred to more than a million per cubic meter of atmosphere. The closer you get to the Earth's surface, the more abundant they become. Icing nuclei are so abundant on the surface that ice normally forms as soon as the temperature drops below the "freezing point". This factor has given rise to the common (but fallacious) belief that water automatically freezes when this freezing point is reached.

Statistical mechanics tells us that some agglomerations of water molecules will possess sufficiently low kinetic energies that the forces of attraction will cause their hydrogen atoms to start to align in proto-crystal arrangements. This is the start of the freezing process.

At standard atmospheric pressure, this process usually starts when the water temperature drops below 3.984°C. This is the temperature at which liquid water has its maximum density. As the water cools past this point, proto-crystal structures begin to appear in greater and greater numbers. Since these structures have greater volume per unit mass than unstructured water, the density of the water mass decreases.

The significance of ionization in the freezing process cannot be overlooked. At water temperatures approaching 0°C, the number of "icing ions" begins to increase. These are hydronium ions (H_3O^+) with six bonded water molecules attached, making a $H_{15}O_7^+$ structure. This hexagonal structure is not electrostatically saturated, and readily bonds and tessellates throughout a mass of cooling water. If conditions are right, the liquid water thus turns to ice.

Summary

Ice readily and spontaneously melts whenever the ambient temperature rises to the melting point—usually around 0°C. That melting point depends upon the ambient pressure and the presence and concentration of solutes in the ice.

Water, on the other hand, does not spontaneously freeze when the ambient temperature drops below the melting point of ice. It can and does remain liquid at temperatures of -40°C and more. Before freezing can take place in this range of -40° to 0°C, icing nuclei are required.

These icing nuclei are abundant on the earth's surface, but become rarer at higher elevations. This enables the formation of winter clouds, whose water droplets easily endure temperatures tens of degrees below the melting point of ice.