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ICE — THE COMMON, YET STRANGE SUBSTANCE

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Who Studies Ice?

Certainly a common feature of the Iowa winter landscape is a solid form of water. Since it is so common, most researchers in ice find even other scientists surprised that one would still be studying ice. Surely most things of significance are known about that mundane substance!

Ice has been the focus of studies by physicists, chemists, geologists and even biologists for many years. Ice represents a basic example of the hydrogen bond which is present in many important organic molecules. In some parts of the world, ice or permafrost is an important constituent of construction. The movement of glaciers and formation of hailstones represent aspects of ice physics. Cell water in living cells appears to be ice-like. However, ice is still not fully understood. An international conference on the physics and chemistry of ice is held approximately every four years.

Ice is a Bit Strange

Ice has a number of unusual properties. Everyone knows that water is quite extraordinary in that it expands on freezing causing ice to have a smaller density than water. Consequently ice floats on water; if this were not true the winter ecology of lakes and streams would be quite another matter.

The reduced density of ice is the result of the open lattice structure which the H_2O molecules assume when water freezes. At ordinary pressures the lattice structure is hexagonal, in a sort of honeycomb structure as shown in Figure 1. There is a lot of space between molecules in this structure, so that the molecules are not as closely packed as they are in the liquid state.

In fact, there are 7 (now possibly 8) forms of ice which are known to exist at various pressures and temperatures. This is more than is known for any other substance. The symmetry of the common ice (Ih form) is evident in the beautiful patterns of snowflakes. Even here there is a bit of a mystery. In the formation of a snowflake, how does a spire growing on one side of the flake know about the particular shape and direction of those on opposite sides?

Structure of the Ice Lattice

The hexagonal form of the oxygen lattice was discovered through x-ray diffraction by an Englishman, W. Bragg, near the beginning of this century. However, the location of the hydrogen atoms is not revealed by this

technique, due to their small size. Other evidence (*e.g.* infra red spectra) indicates that the H_2O molecule is substantially intact in the ice structure. Bernal and Fowler¹, in 1933, proposed that one hydrogen nucleus lies on the bond between every pair of oxygen atoms (but closer to the oxygen with which it is associated). The positive charge of the hydrogen nucleus binds a pair of negative charged clouds from oxygen atoms together, forming the hydrogen bond. There are four close oxygen neighbors to each oxygen atom, thus two hydrogens are supplied by the given H_2O molecule, and two are supplied by other molecules (see Fig. 1). A great many hydrogen configurations can be made by obeying these simple rules. Linus Pauling², in 1935, proposed that this randomness of the hydrogen sublattice causes the observed *residual entropy* in ice. Earlier heat capacity measurements on ice had revealed that there is some sort of disorder (or entropy) remaining in an ice crystal, even as it is cooled to temperatures approaching absolute zero.

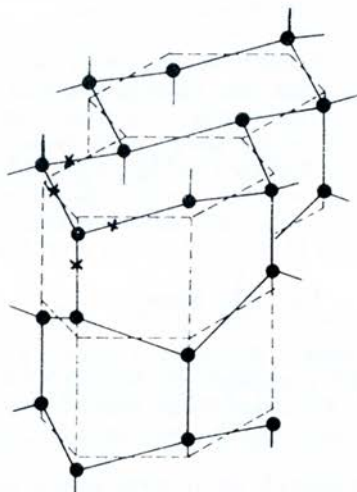


Figure 1. The hexagonal symmetry of the oxygen lattice of common Ice Ih is illustrated. The solid circles represent oxygen positions. Allowable hydrogen placement for two H_2O molecules is illustrated by the X's placed on O-O bonds.

There is Traffic in the Ice

During the early part of this century it was also discovered that ice has a significant dielectric constant. The H_2O molecule has a permanent charge separation in connection with its *benf L* shape. When placed between the charged plates of a capacitor, these electric dipoles are capable of lining up along the electric field in some hundred microseconds. This is called the *dielectric relaxation* time of the material. It is clear that there is a significant and rapid molecular motion in ice.

However, not until 1951 was there a particular model advanced for just what the motion might be. A Danish chemist³, Niels Bjerrum, postulated two types of lattice defects could be responsible. His *orientational defect* has the H₂O molecule rotating about one O-H leg, so that the other hydrogen nucleus leaves its normal bond and moves to an already occupied O-H-O bond. The result is a double occupied bond (O-H-H-O) and an empty bond (O-O). These abnormal bonds may then move through the lattice as subsequently influenced H₂O molecules rotate.

The other defect which Bjerrum postulated is reasonably familiar. We know water ionizes to some extent to H₃O⁺ and OH⁻ ions. It is possible that a proton may move across a bond to form an H₃O⁺ ion and leave behind an OH⁻ ion. These ions may further propagate through the lattice as a different proton (H nucleus) of the H₃O⁺ ion leaves its host to ionize yet another neighbor. (Nobel Laureate Nels Onsager refers picturesquely to the *traffic in ice*.)

Let's "Muddy" the Ice

The problem which arises is that of deciding just what the nature of the motion and the defects might be in ice. One technique used is to "muddy the water" a bit, so to speak. Impurity molecules are added to ice in an effort to gain some insight into what is happening; this is referred to as *doping* the ice with impurities.

In 1957, the Swiss physicists Granicher and Steinemann⁴ added hydrofluoric acid (HF) in very small amounts to ice (a few parts per million), and observed a pronounced effect on ice motion as evidenced by the dielectric relaxation. Because of the similar sizes and orbital structures of fluorine and oxygen, they hoped HF would fit into normal H₂O positions in ice. The dielectric relaxation time was found to be significantly shortened which indicates increased molecular motion. This was explained by the view that since HF (and not H₂F) is the nature of the impurity, an automatic empty bond (O-O) defect is introduced in ice for each HF molecule added. That is, one H atom for bonding purposes is missing for each HF molecule introduced into the ice lattice.

NMR and Ice

There are other techniques which may be applied in an effort to understand the nature of ice defects. One is *nuclear magnetic resonance* (NMR), which was discovered in 1948 by Bloembergen, Purcell and Pound at Harvard University, and independently by Block, Hansen, and Packard at Stanford University. In fact, Bloembergen⁵ investigated pure ice a bit in his pioneering work. Pulsed NMR came later, and is easier to appreciate in some respects. The nuclei of hydrogen (and a number of other nuclei) act like tiny

compass needles--magnetic dipoles. When placed between the pole faces of a laboratory magnet they tend to align along the magnetic field. This is the preferred situation (lowest energy configuration). When radiofrequency electromagnetic radiation at the proper resonance frequency is applied, the nuclear dipoles absorb energy and tip away from the aligned direction. They will then slowly give up energy and line up again with the magnetic field; the time involved is called the *spin-lattice relaxation time* (T_1). One of the ways they may give up energy is through the fluctuating tiny magnetic fields caused by neighbors in motion. Thus, NMR can be sensitive to molecular motion.

Ice Experiments at Luther College

At Luther College during the past few years, we have carefully studied the NMR T_1 of HF doped ice as a function of temperature. The pulsed NMR equipment was designed and constructed at Luther, and includes a minicomputer to acquire and analyze data. In either pure ice or HF doped ice the molecular motion increases as the temperature is increased and the T_1 time is reduced. The change, as a function of temperature, occurs more rapidly in pure ice than in HF doped ice. Consequently there is a combination of HF doping and temperature where the motions produced by pure ice defects and by HF molecules are equal in their effect on the NMR T_1 .

If the defects introduced in ice by HF are the same as those occurring naturally in pure ice, there should be an interaction between the populations of defects. The mass action law (which describes equilibrium concentrations in chemical reactions as well as crystal defect populations) requires that the artificial defects should suppress the population of corresponding natural defect pairs. Examination of our NMR data shows no such interaction at low to medium concentrations of HF ($1:10^7$ to $1:10^5$ HF to H_2O molecular ratios).

We conclude that the pure ice defects responsible for NMR detected motions are different from the motions produced by HF impurities. The picture we propose at the present time is that the pure ice defects which most influence the NMR T_1 are lattice vacancies; that is, actual holes in the lattice where H_2O molecules are missing. H_2 molecules move as they jump into nearby holes. In addition the HF molecule may be producing the different types of defects proposed by Bjerrum. We are currently experimenting with other types of impurity atoms in ice in an effort to establish more definitely the nature of the motions occurring in pure and doped ice.

Does it Matter to Anyone?

Several applications of this knowledge may be cited. The nature of defects in ice is important because they determine the plasticity of ice--that is, the rate of movement of ice in glaciers. Quite recently acids in ice have become a concern of Norwegians. Industrial pollution from Europe is falling from the

atmosphere and is being incorporated into snow. The acidity of the streams is raised as the snow melts, and kills the beloved trout and salmon in the streams. Therefore more knowledge of how acids are incorporated into ice is desirable. Further, since hydrogen bonding is so important, it is desirable to understand the basic and significant case of ice as completely as possible. And of course, who knows when knowledge from basic research may become important to mankind?

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MCA AWARD

The Manufacturing Chemists Association (MCA), again in 1978, will present awards to high school, two-year and four-year college chemistry and chemical engineering teachers.

Since 1957, MCA has honored teachers with national awards of \$1,000, a medal and a citation. MCA will honor two-year college and high school teachers also with regional awards of \$400, a medal and a citation. Chemistry and chemical engineering teachers in the United States and Canada may be nominated. A minimum of 10 years teaching experience is required for the national award.

Winners will be chosen on the basis of teaching excellence, motivation of students to careers in chemistry and allied fields, dedication to science instruction and scholarship, and the ability to highlight the relevance of chemistry to society and good citizenship.

Nominations for the awards must reach MCA no later than Feb. 1, 1978. Winners will be notified on or about April 1 or next year. Further information and nomination forms are available from Dr. Robert E. Varnerin, Manager of Education, Manufacturing Chemists Association, 1825 Connecticut Avenue, N.W., Washington, D.C. 20009.