Reports

Superdense Water Ice

Abstract. *A new allotropic form of water ice with a density of 2.32 ± 0.15 grams per cubic centimeter has been observed at very low pressures and for temperatures lower than 100°K. It is most likely amorphous.*

With the cometary nucleus in mind (*1*), we have studied the morphological behavior of low-temperature snows and ices of water and of clathrate hydrates. An apparatus was set up mainly to measure the apparent low density of snows formed at low temperature and low pressure. The basic apparatus consisted of a copper cone, cooled with refrigerating liquids and placed inside a vacuum chamber with a window through which observers could take photographs.

Distilled water was outgassed, weighed, and conducted to an introduction chamber where it vaporized. The residual pressure of the water vapor in the main chamber was maintained at 10^{-4} mm-Hg or less. The main chamber was then cut off from the vacuum pump and checked for leaks. Water vapor was introduced through a valve at a selected rate. During condensation, the pressure was maintained at 6 to 8×10^{-3} mm-Hg in the main chamber by controlling the rate of introduction of water vapor. Ice or snow was observed as it condensed on the cone. Condensation was stopped by discontinuing the introduction of water vapor and allowing the pressure drop to equilibrium. The apparent volume of the snow or ice was then computed by superimposing the photographs of the cone with and without its ice layer. The perfect symmetrical distribution of the ice was repeatedly checked visually.

At temperatures higher than 120°K, ordinary snow appears, and its apparent density is accordingly very low. With high rates of introduction, very compact snow, whose density (0.93 ± 0.03 g cm^{-3}) approached that of ordinary ice, was produced at 200°K; but at temperatures near or below 100°K, a new form of ice with very high density was produced. The apparatus was then slightly modified to ensure against loss of water during the experiment. It is now possible to re-collect the whole amount of water used and its weight is within 0.1 percent of the initial weight.

In the production of the high-density form of ice, the condensing rate does not seem very critical (Table 1). (The lowest and the highest condensing rates were in the ratio of more than 1 : 20.) However, the temperature of the condensing wall does seem to be critical: no pure glassy high-density ice was produced at temperatures higher than 98°K. The whiter appearance of the ice at 100° and 103°K is believed to mean that the high-density ice was polluted by some low-density ice or snow.

The slightest trace of an impurity, such as methane or air left in the vacuum chamber at an initial pressure of 10^{-4} mm-Hg, stops the apparition of a pure high-density ice; the ice produced is then whiter and has a density of 1.4 to 1.7 depending on the amount of impurity present. It is suggested that a mixture of the high-density ice with clathrate hydrates of methane or of nitrogen and oxygen is formed in this instance.

Thick layers are difficult to build up for another reason. The temperature of the growing layer on the outside surface of the ice cannot be easily controlled for thick layers, and often the high-density ice disappears under a new layer of ordinary snow crystals, probably because of the establishment of a temperature gradient through the layer. This usually happens when the thickness of the high-density ice reaches more than 0.3 mm. This limits the accuracy of the density measurement.

Table 1. Production of the high-density form of ice at various temperatures and rates of condensation.

Temperature (°K)	Rate of condensation (10^{-6} g cm^{-2} sec^{-1})	Density (g cm^{-3})	Appearance
93	40	2.32	Glassy
95	72	2.47	Glassy
95	100	2.23	Glassy
98	920	2.36	Glassy
100	145	2.00	White
103	33	1.30	White

Consideration of all the causes of error gives a density of 2.32 ± 0.15 g cm^{-3} as a weighted average for all the experiments in which contamination by other ices was avoided. This value is surprising because it is considerably higher than the highest densities reported for ice, even for its highest pressure forms. For instance, at pressures higher than 2000 atm, ice VI reaches 1.13 g cm^{-3}, ice III reaches 1.14 g cm^{-3}, and ice II [which occupies the lowest-temperature portions of the high-pressure field (*2*)] reaches 1.17 g cm^{-3} (*3*).

The two low-pressure crystalline forms of ice known between 273°K and 140°K have practically the same density (0.94 g cm^{-3} near 140°K). For this reason, we did not try to distinguish ordinary ice I_h (hexagonal ice) from ice I_c (cubic ice) in our experiments. At low pressure, no high-density ice has ever been described, to our knowledge. However, by condensing a very thin layer of pure water vapor on a surface maintained below 113°K, Burton and Oliver (*4*) observed an x-ray diffraction pattern showing, instead of the many lines given by the hexagonal ice lattice, only two broad and diffuse lines. These lines have been observed later by x-ray or electron diffraction (*5, 6*) and were attributed to a new ice of uncertain structure, which undergoes an irreversible change to cubic ice at higher temperature (*7*).

If Burton and Oliver have produced the same ice, our results confirm arguments (*6*) for the existence of an amorphous or vitreous ice. The observed spacings that correspond to the two broad lines in the diffraction pattern are 3.7 Å and 2.1 Å (*4*). If 2.1 Å is the closest possible packing distance of water molecules, the upper limit for the density of water molecules packed at random in an amorphous configuration lies near 3.25 g cm^{-3}. Although the measured density is not as high, the value found suggests that we have observed a truly amorphous ice, and not semiamorphous ice with a layer structure (*7*). Yannas (*8*) predicts a vitrification at 127° ± 4°K for water, from the depression of vitrification of glycerol by the addition of water. Our measurements are not done at thermodynamic equilibrium and therefore do not exclude such an upper limit for the domain of amorphous ice.

Finally, it is difficult not to mention here the form of liquid water with unusual properties and an unusually high density (1.33 g cm^{-3}) (*9*), a true polymer of water (*10*). It does not seem that this polywater, which solidifies at −40°C into a glasslike state, can be directly connected with our observations.

The superdense form of water ice that we have observed at low pressure and low temperature may play an important role in planetary and cometary physics as well as in interstellar grains, as it is likely not to have the same optical or physicochemical properties as ordinary ice, such as refractive index, albedo, vapor pressure, conductivity, and so forth. However, its importance may be deemphasized in some respects because impurities seem to stop its apparition and its growth.

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References and Notes

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Mechanochemical Turbine: A New Power Cycle

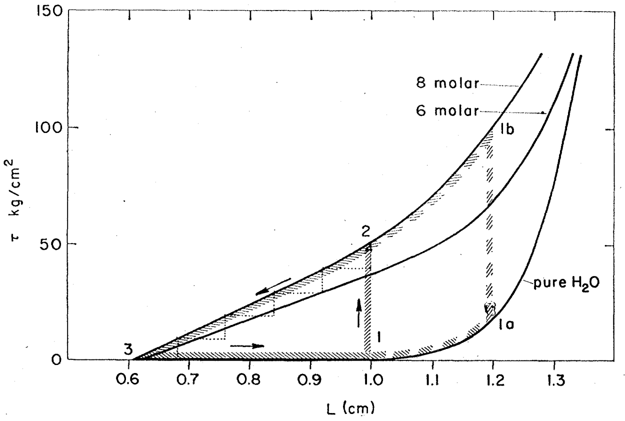
Abstract. *A basic thermodynamic cycle for the production of mechanical power from materials that may be made to contract forcibly and reversibly is described. The cycle differs from existing mechanical power cycles which generally employ expanding fluid as working substances. A "contraction turbine" operating on this cycle has been devised, which has collagen fiber as its working substance and salt solution as fuel and produces mechanical work directly from chemical free energy. Direct conversion of chemical to mechanical energy is routinely effected in muscle but not in usual man-made engines.*

The direct conversion of chemical free energy into mechanical motion is routinely effected in muscle but does not occur in usual man-made engines. In this laboratory mechanochemical engines have been built which do effect the direct conversion (*1*). We now describe a basic thermodynamic cycle for effecting direct conversion of chemical to mechanical energy. The cycle provides a general method for the production of mechanical power from any material which may be made to contract forcefully and reversibly. We have devised a new engine operating on this cycle whose features are basic for efficient production of mechanical work from contractile (rather than "expansile") working substances. (In mechanical power cycles expanding fluids are normally used as working substances.)

In the new engine, which we call a "contraction turbine," regenerated collagen fiber (*2*) cross-linked by formaldehyde is used as working substance, with the reversible contraction that the fiber demonstrates when immersed in concentrated aqueous salt solution, such as LiBr, $CaCl_2$, $MgCl_2$, and KSCN, producing mechanical shaft work.

Figure 1 shows the variation of force (per unit of dry cross-sectional area) with length of collagen fiber in contact with aqueous solutions of LiBr at various concentrations (*3*). At zero tension the specific length of this particular collagen fiber in 8*M* aqueous LiBr solution (L_0) is 60 percent of its specific length in water (L_w). A tension of 52 kg/cm^2 of cross-sectional area is required to maintain the salt-treated fiber at its salt-free length (L_w). The fiber can be repeatedly moved between states on Fig. 1, by subjecting it to the indicated salt concentration and tension, although some degeneration of fiber properties occurs after 100 or more cycles.

These characteristics of collagen in LiBr (and in similar aqueous salt solutions) are exploited to produce mechanical work continuously by subjecting the collagen to the ideal cyclical



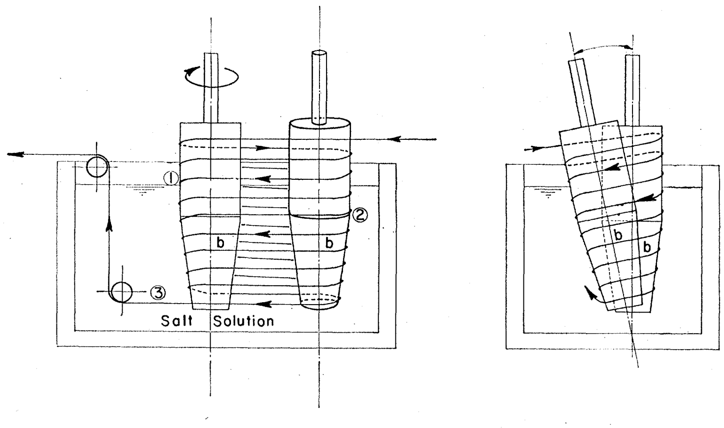


Fig. 1 (left). Tension-length dependence of collagen fiber in LiBr (*2*). Fig. 2 (right). Contractile fiber-actuated turbine. Front and side views. Fiber tension builds up on cylindrical spindle sections between (1) and (2) at constant specific length. Stepwise contraction occurs between (2) and (3) as the fiber helix descends the conical portions of the spindles (*b*).