Entropy decreases with decreasing temperature due to an increase of the local order following the hydrogen bond formation. Similar arguments to those developed above explain the minimum of the temperature dependence of heat capacity.

A more complete discussion of these effects has been done and gives a good explanation of the enhanced anomalies of water observed at low temperature (1,2). More important to notice is a minimum of the isothermal compressibility at 46°C and a sharp increase of the heat capacity at temperatures close and below the melting point, when liquid water is undercooled. The first corresponds microscopically to enhanced density fluctuations corresponding to the existence of short-lifetime low-density regions in liquid water (3). These regions are formed by molecules strongly bound together. Clearly, the percolation mechanism yields a dramatic increase of the size and number of these regions, explaining, incidentally, why homogeneous nucleation takes place at about the same temperature (about 228 K), as the thermodynamic properties seem to diverge. This temperature is also well above the glass transition temperature of liquid water, which is 136 K. The second corresponds to a rapid decrease of the entropy, which approaches the entropy of the crystal, also around 228 K.

The transport properties of liquid water also have a strongly anomalous behavior, in particular at low temperature (1,2). Properties, such as self-diffusion, viscosity, and different relaxation times, show a strong non-Arrhenius temperature dependence, the characteristic activation energy increasing with decreasing temperature. This also corresponds to the fact that, with decreasing temperature, more bonds must be simultaneously broken to allow the movement of a given molecule. At high temperature, when the number of intact bonds is relatively small, the dynamics is similar to that of classical liquid. As the temperature decreases, the activation energy increases. At very low temperatures it is three times larger than at room temperature. Its value corresponds to the energy necessary to break a larger number of bonds at low temperature.

When water is mixed with another liquid, the number of bonds can increase, for instance, in water-ethanol solutions (structure formers) or decrease (structure breakers). However, in all cases, the tetrahedral structure vanishes (except, of course, for isotopic mixtures of light and heavy water). As a consequence, the anomalies of liquid water are strongly reduced upon addition of other components. For instance, 7% of ethanol is sufficient to completely suppress the maximum in the temperature dependence of the density of the mixture (9).

A more detailed study of the properties of water solutions is clearly of major importance in many applications. One can say that it is impossible to speak about a general behavior. Different compounds solubilized in water correspond a priori to different local structures. A very extensive study of salt solutions has been done by Enderby and coworkers (46). Careful neutron-scattering experiments allow the determination of the water shell around several ions. Around a cation, the water molecule is oriented with the oxygen more close to the cation corresponding to a minimization of the energy between the ion and the water dipole. Instead, around an anion, the hydrogen atoms are closer to the ion. The coordination numbers, that is, the number of water molecules that are present inside the first hydration shell and the lifetimes depend very much on the nature of the solute and on its concentration. Around hydrophobic molecules, such as methane, water forms large cages, (clathrates)