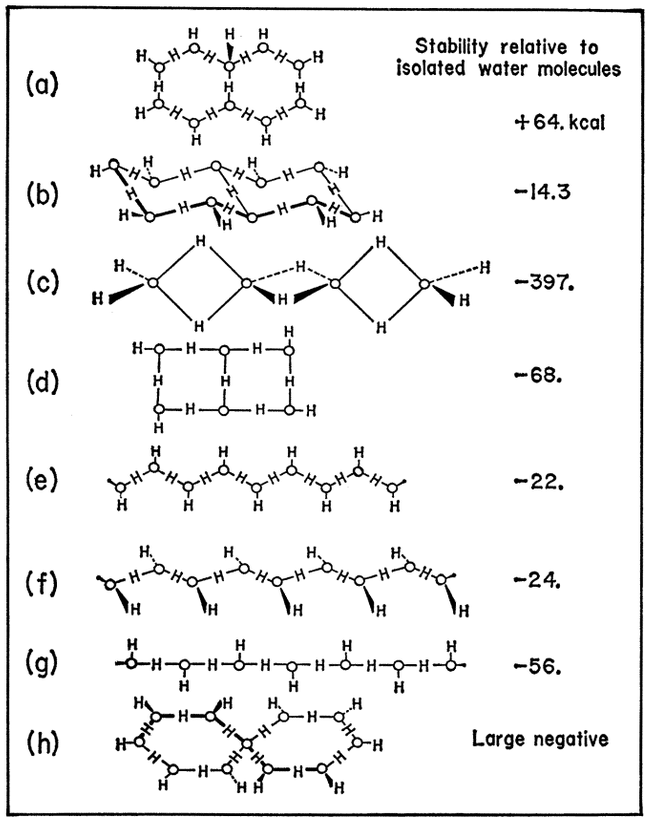
Symmetric hydrogen bonds give form to anomalous water

Debate rages over experiments, but theory shows it can exist



Science

Symmetric hydrogen-bonded structures for anomalous water; (a) is best.

Water is a model for structural chemistry, since its structure depends on hydrogen bonds in which hydrogen shares its electrons with atoms of other elements. This sharing binds them together. Hydrogen bonds are important in the structure of many other compounds, including most alcohols and acids.

If these bonds can make anomalous water—with a molecular weight several times that of ordinary water and a viscosity between that of heavy motor oil and molasses (SN: 12/21/68, p. 616)—the implication is that they can make anomalous forms of these substances too.

This, in part, explains the interest anomalous water has held for chemists since its reputed discovery in 1966. The rest of the explanation is the lure of an unexplained phenomenon.

The existence of anomalous water is still subject to vigorous debate among chemists. It can be made only in minute quantities in tiny capillary tubes.

Some chemists think it too ephemeral for belief; others think it is not a form of water at all but some corrosion product.

But Dr. Leland C. Allen and Peter Kollman of Princeton University believe sufficiently in its existence that they have derived a theoretical prediction of the structure and properties of anomalous water from the basic equations of structural chemistry.

The result gives anomalous water a three-dimensional structure which for the first time incorporates elements experimenters reported seeing. In the new configuration, water molecules form sheets of hexagons that are bound by vertical bonds into three-dimensional structures.

This pattern goes beyond one suggested by an experimental group led by Dr. Ellis R. Lippincott of the University of Maryland (SN: 7/12, p. 23). "We couldn't interpret too much farther than hexagons," says Dr. Lippincott, "Allen has shown they can be linked vertically. On the whole we're quite happy."

The derivation does not prove completely that anomalous water exists, says Dr. Allen. "Theoretical chemistry cannot predict with total confidence," he says, but it shows that a substance with this structure can exist and that it will have many of the properties experimenters record for anomalous water.

"In principle, the stuff should exist," he adds.

Basic to the structure derived by Dr. Allen and Kollman is a new kind of hydrogen bond whose existence was suggested from experimental evidence by Dr. Lippincott and his associates. Ordinary hydrogen bonds that join liquid water molecules to each other have two oxygen atoms with a hydrogen placed asymmetrically between them. Such a bond gives an irregular structure to liquid water.

The new kind of bond, by contrast, has the hydrogen symmetrically placed between the two oxygens and this can give regular structures to anomalous water.

Since the symmetric bond is not much stronger than the asymmetric one, it became a serious question whether any of the possible arrangements of symmetric bonds would produce a structure more stable than ordinary liquid water. Dr. Allen and Kollman studied a large number of these, and they conclude that only one, a cyclic hexagonal arrangement, will do.

But even in that one the difference in stability is marginal. As a consequence, anomalous water needs glass or quartz tube walls as a catalyst.

The tube surfaces, if they have not been wet by ordinary water, will have pairs of hydroxyl radicals (OH) attached. These will attract water molecules from a vapor introduced into the tube and cause them to form cyclic hexagons. At first the hexagons will have ordinary asymmetric hydrogen bonds. After a few of them form, vertical connections between adjacent sheets will be made. At this point the bonds in the hexagons will shift to the symmetric form. After a blob of anomalous water has formed, it can drift away from the tube surface.

Similar cyclic hexagons could form for many other hydrogen-bonded substances, the calculation shows, though for some, stability would favor the ordinary forms. Experimental evidence exists for a hexagonal form of hydrogen fluoride, and there are forms of acetaldehyde and carbon disulfide that have properties similar to anomalous water.

But interest in other anomalous forms is slow. "Water is the name of the game right now," says Dr. Allen. After anomalous water is definitely established, he says, people will go looking for other substances. □