

Polywater

The article "Hydrogen-bond stereochemistry and 'anomalous water'" by Barclay Kamb (1) is valuable because it illustrates how far one can go in predicting the properties of a radically new material on the basis of empirical knowledge about existing compounds. It is also a polemic in the sense that he makes 64 derogatory references to our article (2) while he ignores the contents of, but acknowledges having read, another article of ours (3) which clarifies many of his questions.

1) Those interested in polywater are referred to the special Lehigh Symposium issue of the *Journal of Colloid and Interface Science* that is to be published this September (unfortunately, the printing of these papers comes over a year after the Symposium at Lehigh University on which they are based). This collection is comprised of articles from the scientists who have been principally concerned with this phenomenon—both the believers and nonbelievers—and, in particular, it contains our second article (3).

2) Kamb has chosen the often useful approach of extrapolating existing empirical knowledge on hydrogen bonds to see whether this was consistent with the properties ascribed to polywater. This approach does not, however, provide scientific basis for Kamb's dismissal of the quantum mechanical calculations that we and a number of others have made.

3) One of Kamb's principal theses was that if polywater existed, it should have tetrahedral coordination. Our own and other calculations show a clear-cut preference for planar over tetrahedral geometry. This result has a simple electrostatic origin and holds even if one does not have high confidence in quantum mechanical calculations.

4) Another major point is Kamb's claim that the existence of stable H_5O_2^+ , with its known short symmetric bonds, would provide an activation mechanism for eliminating a kinetic barrier between symmetric and asymmetric bonds. However, the type of symmetrically bonded structure and origin of kinetic barrier that we origi-

nally proposed bears little resemblance to H_5O_2^+ or its suggested action.

5) Kamb has introduced, and then discredited, more attributes to our diamond-graphite analog than were given or implied in our first article. Our almost parenthetical comments referred simply to packing and the observation that two forms of a material with rather similar energies seemed to exist for both cases.

6) Kamb has generated confusion as to our present stand on the existence of polywater. We now believe that a new water allotrope does *not* exist. This evaluation arises neither from the various experimental papers claiming to disprove it (because there is reason to question the care taken to eliminate impurities and because of the strong disagreements among the experimenters themselves) nor from Kamb's arguments, but rather from three other lines of reasoning: (i) high-accuracy ab initio calculations on cyclic, symmetric bonded water molecules show that this type of bond possesses a much higher energy than the normal asymmetric type and other calculations which demonstrate a short-range wall effect; (ii) a new measurement by Deryagin indicating a molecular weight of approximately 180, a value that is inconsistent with our original model; and (iii) the failure of Lippincott, Stromberg, Grant, and Cessac (4) to reproduce their Raman spectra and the lack of precise uniqueness in their infrared spectrum.

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References

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Kamb (1) has recently dismissed the rhombic dodecahedral model suggested (2) for "polywater." He states that it "provides a reasonable tetrahedral bonding geometry for eight of the 14

oxygen atoms of the unit, but the coordination of the remaining six oxygen atoms is highly abnormal." Kamb further states that at these six oxygen atoms there are "four $\text{O}\cdots\text{O}\cdots\text{O}$ bond angles of 60° " and points out that "Donohue omitted the 60° bond angles in his description of the structures" [emphases added].

Of course I omitted mention of these angles because the central oxygen atom in these groupings is the donor not of two hydrogen bonds (with the implied small $\text{H}-\text{O}-\text{H}$ angle), but of only one, and the angle subtended at the central atom in such systems is of no structural significance. Furthermore, it is not true, as asserted by Kamb, that "the acceptor relation involving 60° angles is quite unsatisfactory." A geometrical lapsus has occurred here, because the angles in question are not 60° , but in fact $70^\circ 32'$. Even so, does this distortion from tetrahedral represent an unacceptable situation? Now, sp^2 - sp^3 hybridophiles to the contrary, an acceptor oxygen atom does not impose restrictions on the relative geometry of the incoming hydrogen bonds (3). An additional example is found in the crystal structure of urea (4), where each oxygen atom accepts four hydrogen bonds; the six acceptor angles at the oxygen atom are 45° (one), 72° (four), and 131° (one). Thus, angles of $70^\circ 32'$ are not only not unreasonable but not unprecedented.

I conclude that the rhombic dodecahedral model for "polywater" cannot be rejected for the reasons given by Kamb. The other considerations in Kamb's article are outside the scope of this note.

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References and Notes

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