Hydrogen-Bond Stereochemistry and "Anomalous Water"

The "polywater" controversy prompts a close look at novel kinds of H-bonding.

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Structural features proposed recently for "polywater" or "anomalous water" (*1–12*) represent a significant broadening of the stereochemistry previously recognized for hydrogen bonding by water molecules. The existence of an H_2O phase with the proposed features would require important revisions in thinking about the nature and properties of water (*13*, pp. 464–473; *14–16*). Although doubts have been expressed about the experimental basis for "anomalous water" (*17, 18*), published structural theories (*1–12*) nevertheless appear to provide a rational basis for the existence of an H_2O phase with the properties reported (*1, 3, 8, 19*). My purpose here is to single out the novel features of H-bond stereochemistry proposed in these theories, and to examine them in the light of empirical evidence and existing ideas about the bonding forces between water molecules. The somewhat unusual aspects of H-bond stereochemistry that must be considered in examining the proposed theories in this way are those that define some of the limits of flexibility in H-bonding interactions, and thus have significance not only for hypothetical "polywater" structures, but also for the structure and properties of ordinary water and other H-bonded systems. Reexamination of ideas of H-bonding that bear on these important subjects is a useful outgrowth of the controversy over "anomalous water," however the experimental questions concerning this material are finally resolved.

Structural theories for "anomalous water" as a pure H_2O phase are summarized in Table 1. The molecular models in references (*1–8*) are proposed on purely geometrical grounds, without quantitative justification of their stability. Qualitative features of electronic valence-bond structure in relation to the proposed models are considered in references (*5*), (*8*), and (*9*). References (*9–12*) involve quantitative quantum-mechanical calculations. All of the structural models for "anomalous water" or "polywater" call on polymerization of water molecules by H-bonding (*20*). In the models of references (*1–4*), the proposed H-bonds are asymmetric, and the proposed molecular models can be examined straightforwardly in the light of information about the known condensed phases of H_2O, in which the same type of bonding occurs. For the models of references (*5–12*), in which the proposed H-bonds are symmetric, the known H_2O phases do not give direct information, but an indirect basis for examining these models is provided by valence-bond concepts and by experimental data on substances containing symmetric O–H–O bonds, particularly those between water molecules.

The existing structural information and stereochemical concepts provide the standard used here in assessing the reasonableness of proposed structures for "anomalous water," and on this basis, only a few of them are found acceptable. For these few, the question of possible metastability in relation to ordinary water is of first importance. It proves possible to assess the barriers for conversion of these structures to ordinary water, and to set a lower limit on the energies of these structures, again on the basis of experimental information from known H_2O phases. The outcome of these assessments is a definite denial of the proposed structural basis for "anomalous water." Since this conclusion rests squarely on existing concepts of H-bond stereochemistry, the considerations presented here show in some detail where these concepts would have to be abandoned or modified if the existence of structures of the type proposed for "anomalous water" were to be verified experimentally.

Asymmetric H-Bonding

The polymerized structure proposed by Deryagin (*1*) is ice-like, with cavities containing non-H-bonded, "anomalous" molecules; this model is similar to the interstitial model for ordinary liquid water (*14*, p. 189; *15; 21*), but differs in the assumption that cavity occupancy is an independently variable compositional parameter and can be increased in "anomalous" water. This assumption conflicts with the reversible microscopic equilibrium between framework and cavity molecules in the interstitial model of ordinary water (*14*, p. 189; *15*; *21*). It also conflicts with the presence of only one type of dielectric relaxation process for molecules in liquid water, averaged over times of the order of 10^{-11} second (*22*).

Erlander (*2*) proposes an ice-like H-bonded structure of the type present in ice II, one of the high-pressure forms of ice. Although the density of ice II, 1.18 grams per cubic centimeter, is too small to account for reported "anomalous water" densities as high as 1.4 grams per cubic centimeter (*17*), other high-pressure ice phases have densities that range up to 1.5 grams per cubic centimeter (*23*); hence structures of these types may be considered. The role of the dense ice structures in the decrease of volume on melting and in other properties of ordinary liquid water has been discussed (*16*). However, there is no basis for assuming the existence, at room temperature and atmospheric pressure, of only one of these dense structures individually as a stable or metastable phase. All are unstable relative to ice I or liquid water at atmospheric pressure, and the molecular mobilities in the ice structures are sufficiently great that the dense phases can be maintained metastably only below −100°C (*24*). In liquid water, however, the collective configurational entropy of many different molecular arrangements, in equilibrium at the

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microscopic level, is available to stabilize some denser configurations in competition with the energetically more favorable arrangement of ordinary ice I. Under pressure, densification of the liquid is achieved in large part by an increased abundance of the denser molecular arrangements, which probably resemble the structures of the dense solid phases (*16*). If one of these dense arrangements represented the "anomalous" component, application of high pressure to ordinary water should provide a method for making "anomalous water," but experiments designed to do this have failed (*25*).

Bellamy *et al.* (*3*) and Bolander *et al.* (*4*) propose water tetramers. The square tetramer of Bellamy *et al.* (*3*) occurs in ices V and VI (*16*) and in some clathrate hydrates (*26*). However, the H-bond lengths are 2.80 to 2.82 angstroms, rather than being greatly shortened from 2.76 angstroms, as Bellamy *et al.* (*3*) assume would occur. The argument given for shortened H-bonds, based on reduced repulsion between lone pairs (*3*), does not appear affected significantly by the fact that the tetramers in ices V and VI and in the clathrate hydrates are H-bonded to other water molecules, and that the tetramers are not all strictly planar. The tetramer proposed by Bolander *et al.* (*4*) is tetrahedral. This H-bonding geometry does not occur in any ice or hydrate structure (*27*); even individual trimers (corresponding to the faces of the tetrahedron) do not occur (*16, 26*). On the basis of the energetics of H-bond bending (*16*), the bond energy for tetrahedral tetramers is reduced by at least 1.2 kilocalories per mole from that for the most highly bent bonds that occur in any known ice phase (O···O···O angle of 76°). Since dense ice phases with bond energies only 0.1 to 0.5 kilocalorie per mole less than those in ice I require pressures above 2000 atmospheres for stabilization, and cannot be held metastably at 1 atmosphere except below −100°C, and since the molecular mobility increases with increased H-bond bending (*16*), the tetrahedral tetramer should not occur either stably or metastably under ordinary conditions.

Symmetric H-Bonding

The proposal of short, symmetric O–H–O bonds in "polywater" (*5–12*) is surprising, because none of the known solid H_2O phases, even those denser than the "anomalous" material, have such bonds (*23*). The increased densities of the known phases are achieved not by bond shortening, but by bond bending and by the "self-clathrate" feature; the H-bonds are actually longer and more asymmetric than in the low-density forms. One asks why the proposed symmetric H-bonds do not occur among the known stable dense forms of H_2O, particularly if these bonds are stronger than asymmetric bonds by as much as 50 kilocalories per mole, as proposed by Lippincott *et al.* (*8*). Even if the symmetric bonds are not so strong, conditions would nevertheless have to exist under which the symmetrically bonded structure is thermodynamically stable relative to known H_2O phases, in order for it to form at all. The fact that such a symmetrically bonded structure is not observed to form, except, perhaps, under the proposed catalytic influence of a glass or silica surface, requires the theorists (*5–12*) to postulate a high energy barrier between the symmetrically and asymmetrically bonded structures. Such a barrier is also used to explain the metastable persistence of "polywater" under conditions where it is not stable relative to other H_2O phases (*12*). Existence of this barrier is the primary question in judging the possible validity of these theories, but it is best discussed after considering some geometrical features of the particular symmetrically bonded structures proposed.

Linnett (*5*) proposes molecular arrangements that are identical to those in ices I and Ic, except that the H-bonds are symmetric rather than asymmetric as in the ices (*28*). One could, in principle, produce these structures by simple hydrostatic compression of ice I or ice Ic. The required O···O distance for symmetric O–H–O bonds is estimated theoretically to be 2.34 angstroms (*13*, p. 484), and is found empirically to be in the range 2.40 to 2.54 angstroms (*29–34; 35*, pp. 119, 182; *36*). The individual O–H covalent bonds in such a structure have a bond number of approximately ½ (*13*, p. 484). Linnett (*5*) gives an interpretation of the electronic structure of these bonds in terms of the "double quartet" hypothesis, which fits well the structural geometry; an alternative interpretation can as well be made in terms of resonating covalent bonds and unshared electron pairs, each electron pair (:) being shared (O:H) and unshared (O: H) half of the time.

In constrast, Donohue (*6*) and O'Konski (*7*) propose structures that bear no relation to any known form of H_2O. The rhombic dodecahedral unit of Donohue (*6*) 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 (*37*). The structural scheme of O'Konski (*7*), which involves pairs of bridging hydrogen atoms between oxygens (*38*), is very similar to what occurs in certain electron-deficient substances (*13*, pp. 368, 380) but not in electron-rich substances, as far as is known. Geometrically, the proposed atomic arrangement could arise by a proton-ordering transition in ice VII (*39*); an ordering transition does in fact occur (to ice VIII), but the resulting proton arrangement is entirely different (*40*). A quantum mechanical calculation (*12*, figure 4c) for a structure geometrically like one of the oligomers proposed by O'Konski (*7*) indicated a large instability relative to free water molecules.

O'Konski (*7*) argues against three-dimensional structures like that of Linnett (*5*) on the grounds that they imply low volatility, but, in fact, low volatility is one of the attributes reported for "anomalous water" (*1, 3, 8, 17*); in any case, the volatility depends on the size of the polymerized aggregate, which has not been definitely specified in most of the theories put forward. On the basis of viscosity, Linnett (*5*) argues that three-dimensional structures are "inherently" more probable than sheet structures.

The Planar Hexagonal Network

The "polywater" structures proposed by Lippincott *et al.* (*8*) and considered further in references (*9–12*) are based on planar hexagonal rings of oxygens, linked by symmetric H-bonds, and connected to form an extended planar hexagonal network. Because a multiple ring network cannot have H_2O stoichiometry without the inclusion of additional protons either attached on the sides of the planar sheets or as independent ions, Lippincott *et al.* (*8*) and Pedersen (*10*) alternatively propose branching, apparently planar chains, which can be neutral or can carry a net positive charge. These structures are derivable from the extended planar ring networks by omission of some of the oxygen and hydrogen atoms. Allen

Table 1. Summary of structural models for "anomalous water."

Reference	Author	Bonds*	Atomic arrangement	Main basis
(*1*)	Deryagin *et al.*	a	Ice I, cavities filled by "anomalous" molecular component	Density; vapor pressure; thermal expansion
(*2*)	Erlander	a	Ice II	Density
(*3*)	Bellamy *et al.*	a	Square ring $(H_2O)_4$ with short H-bonds	Infrared spectrum
(*4*)	Bolander *et al.*	a	Tetrahedron $(H_2O)_4$	Catalytic action of quartz
(*5*)	Linnett	s	Tetrahedral bond network as in diamond or cristobalite	"Double quartet" hypothesis of electronic structure
(*6*)	Donohue	s	Rhombic dodecahedron $(H_2O)_{14}$	Viscosity; stereochemistry
(*7*)	O'Konski	s	Chain polymers with pairs of bridging hydrogens	Non-three-dimensionality of polymer
(*8*)	Lippincott *et al.*	s	Planar hexagonal ring networks of O–H–O bonds; branching chains	Infrared and Raman spectrum; π bonding
(*9*)	Messmer	s	π bonding in planar hexagonal bond network	Analogy with unsaturated hydrocarbons; quantum mechanical calculations
(*10*)	Pedersen	s	Planar ring and chain polymers, neutral and charged	Quantum mechanical calculation of bond orders
(*11*)	Morokuma	s	Planar hexagonal O–H–O ring networks	Quantum mechanical calculation; comparison with asymmetric bonding
(*12*)	Allen and Kollman	s	Planar hexagonal sheets held together by between-sheet O–H–O bonds	Quantum mechanical calculation; comparison of various conformations

* Polymerization by asymmetric H-bonding, a; polymerization by symmetric H-bonding, s.

and Kollman (*12*) propose structures built by stacking the planar ring networks side by side and bonding them together by means of the extra protons needed to achieve H_2O stoichiometry.

By an alteration of the bond angles from 120° to 109.5°, the planar ring networks in references (*8–12*) can be converted to puckered hexagonal sheets that can be stacked one above the other to give the tetrahedrally linked structures of Linnett (*5*). What structural basis is there for preferring the planar hexagonal network to the puckered one that is present in the tetrahedrally linked structures? Lippincott *et al.* (*8*) and Messmer (*9*) give qualitative arguments for the planar network, and Allen and Kollman (*12*) give a quantitative argument based on quantum mechanical calculations.

Lippincott *et al.* (*8*) suggest that the reported density of "polywater" is incompatible with the structures of Linnett (*5*), but this is erroneous: an O···O bond length of 2.40 angstroms, which is experimentally more reasonable than the 2.30 angstroms assumed by Lippincott *et al.* (*8*), corresponds for the tetrahedrally linked structures to a density of 1.39 grams per cubic centimeter, which is within the range reported (*17*). Lippincott *et al.* (*8*) also argue that the experimental failure to produce "polywater" under pressure (*25*) is evidence that it cannot have the tetrahedrally linked structure, since this structure can be obtained by hydrostatic compression of ices I or Ic. This argument is also invalid: ice I transforms reconstructively to denser ice phases at a pressure much lower than that required to symmetrize the bonds by compression (*41*), so that transformation under high pressure to a symmetrically bonded structure of either type (planar or tetrahedral) would necessarily be reconstructive, involving bond breakage; the failure of such a transformation to occur does not preclude a structure of one type any more than the other.

The choice between the planar and tetrahedral structures is, of course, determined by the comparative bond strengths, which are governed by the electronic structures of the bonds. According to Lippincott *et al.* (*8*), the oxygen bond orbitals in the planar structure will be sp^2-hybridized and the O–H bonds will have a bond number of ⅔ (*42*), whereas in the tetrahedral structure the O–H bonds will have a bond number of ½. This comparison carries the implication that the bonds in the planar structure would be four-thirds as strong as the bonds in the tetrahedral structure, which is what would be necessary to make the planar structure (without any contributions from out-of-plane protons) as stable as the tetrahedral one, since per oxygen atom the extended planar structure has only three-fourths as many bonds as the tetrahedral one. To increase the O–H bond number above ½ in the planar structure, Lippincott *et al.* (*8*) call upon delocalization of the unshared electron pair on oxygen. As noted in reference (*9*), this is possible only if a $2p$ orbital of hydrogen is utilized, so as to carry the delocalized electrons and to overlap with the p_z orbital of oxygen, forming a π bond (*43*). However, Pauling (*13*, p. 450) points out that the $2p$ orbitals of hydrogen have negligibly small bond-forming power, owing, first, to the shielding of the nuclear charge from the orbitals of the L shell by the $1s$ electron already present, and, second, to the large inherent energy gap (234 kilocalories per mole of H atoms) between the $1s$ and $2p$ energy levels even in the absence of any shielding. Messmer (*9*) argues the case for π bonding in the planar structure by citing the example of double bonds in unsaturated hydrocarbons, but the situation in these compounds is entirely different, since no $2p$ orbitals of hydrogen are involved. If hydrogen $2p$ orbitals could be used in the proposed planar structure, they could be used equally well in the bond structure of the isolated water molecule, but there is no theoretical or experimental indication of this (*14*, pp. 23–35). Consequently, the suggestion of π bonding must be rejected and the O–H bond number must be taken to be ½ in the planar structure. This conclusion is in agreement, according to Pauling (*13*, p. 484), with the assumed bond lengths of about 2.3 angstroms (*8*, *9*), and it implies that the tetrahedral structure, with more bonds per oxygen, is more stable. Although Messmer (*9*) reports some quantum mechanical calculations that support π bonding, other calculations (*12*, p. 1447) indicate no tendency toward delocalization of the oxygen unshared pairs (*44*).

Stacks of Planar Sheets

Although discounting the importance of π bonding, Allen and Kollman (*12*) nevertheless conclude that the planar ring structures are more stable than the puckered ones, and attribute this to "a new form of bonding" (*12*, p. 1447), whose nature, however, is not clarified by the quantum mechanical results given (*45*). Allen and Kollman (*12*, p. 1447) argue that the charged, strictly planar networks of references (*8, 11*) are untenable, and that chains [as proposed alternatively by Lippincott *et al.* (*8*)] are unstable relative to isolated water molecules (*12*, p. 1447). In place of these, Allen and Kollman (*12*) propose neutral structures built from two or more planar hexagonal networks, and containing, in addition, the necessary out-of-plane protons, which are used to bond together adjacent planar networks (*46*). In the three-dimensional structures thus formed (*12*, figure 1), all or a substantial fraction of the oxygen atoms are 4-coordinated by hydrogen. If the sheets are planar, the coordination polyhedron of oxygen by hydrogen is a far-off-center trigonal pyramid of hydrogen atoms, with the oxygen atom lying in the base of the pyramid. This curious type of far-off-center coordination can be designated "3 + 1." What is the basis for the conclusion (*12*) that the planar networks with 3 + 1 coordination are more stable than puckered networks with tetrahedral coordination?

For structure type C (*12*, figure 1c), consisting of only two network sheets, the planarity of the sheets is forced by the assumed bonding geometry, in which every oxygen of one sheet is bonded to the adjacent oxygen of the other sheet. Puckering of the sheets would require either gross disparities among the intersheet bond lengths or else an even farther off-center coordination for half of the oxygens. Because of this forced planarity, structure C provides no argument for increased stability of the planar over the puckered sheet configuration. On the other hand, the network sheets in structure types A and B (*12*, figure 1, a and b) can be converted to the puckered configuration by a simple adjustment of bond angles, without any change in bond lengths. This constitutes a displacive transformation from structures A and B to the ice I- and ice Ic-like structures of Linnett (*5*). The bond angles change from 120° and 90° to 109.5°, and the cordination of all the oxygen atoms becomes tetrahedral. What stabilizes structures A and B against this transformation?

Allen and Kollman (*12*) argue for greater stability of the planar configuration on the basis of a single comparison of calculated energies, for a "naphthalene-like" double six-ring ($H_{20}O_{10}$) in the planar and puckered conformations (*12*, figure 4, a and b). This molecular group is too small to have any stacking of network sheets, linked by "out-of-plane" protons, although such stacking is an essential feature of structures A and B. Moreover, the chosen disposition of protons in the two "naphthalene" structures studied is such that only one proton out of the 20 is "out-of-plane," and thus only one of the ten oxygen atoms is 4-coordinated by hydrogen (*47*). These features introduce a bias in favor of the planar conformation, because the electrostatic energy is minimized in the planar conformation if there are no "out-of-plane" protons, or if there are so few that their electrostatic energy contributions can be disregarded. The "naphthalene-like" comparison is therefore an inadequate basis for reaching the significant conclusion that the stable conformation of the network sheets is planar.

Observed Oxygen Coordinations

In support of the calculated energy comparisons among different structures, such as planar versus puckered rings, Allen and Kollman (*12*, p. 1444) state that "for systems involving various associations of water molecules, CNDO/2 [the method of quantum mechanical calculation] is acting as a successful interpolation and extrapolation scheme." However, no concrete support for this conclusion is given; there is no indication that the method gives correct relative energies for several associations of known energy, and of complexity comparable to the proposed "polywater" structures or even the "naphthalene-like" example. In reaching a conclusion on the relative stabilities of the planar and puckered sheet conformations, it is better therefore to rely on observational experience. No instance is known in which oxygen forms bonds of equal or even only roughly equal strength to four neighbors arranged in the 3 + 1 type of coordination, whereas there are numerous examples of oxygen forming four bonds in tetrahedral directions. This behavior is a consequence of the directionality of the four covalent bonds, and also of the repulsion between the ligands (*13*, pp. 464–473).

A pertinent example is the structure of Cu_2O (*13*, figure 7–9). The Cu atoms are 2-coordinated, being symmetrically located midway between oxygen atoms. The oxygen atoms are tetrahedrally coordinated, and the O–Cu–O bond network is identical to the O–H–O network in the ice Ic–related structure of Linnett (*5*). The Cu atoms achieve linear 2-coordination by *sp* hybridization, whereas the H atoms can use only the 1*s* orbital, without hybridization. Nevertheless, the Cu_2O structure type is a reasonable one for a symmetrically H-bonded form of H_2O, because the requirements for orbital hybridization for oxygen are the same for four covalent bonds as they are for two bonds resonating with two unshared pairs, as needed to give O–H a bond number of ½ in the H_2O phase. In fact, the Cu_2O structure type occurs in ice VII (*39*), except that the H-bonds are asymmetric at pressures that have been reached so far (*48*).

No actual examples have been found of oxygen 4-coordinated only by hydrogen atoms that form symmetric O–H–O bonds. However, the ions H_3O^+, $H_5O_2{}^+$, and higher aquo hydrogen ions of the type $H(H_2O)_m{}^+$ are examples of oxygen 3-coordinated only by hydrogen atoms, some of which form short H-bonds. These examples provide the closest available observational basis for discussing the proposed "anomalous water" structures with short H-bonds. In $H_5O_2{}^+$ the oxygen atoms are linked by a symmetric or nearly symmetric O–H–O bond of length 2.41 to 2.50 angstroms; the remaining four H atoms form asymmetric H-bonds to adjacent oxygen atoms or other anions (*29–31*). Of the higher aquo hydrogen ions, the only examples that have been studied in detail crystallographically are the $H_7O_3{}^+$ and $H_9O_4{}^+$ groups that occur in $HBr \cdot 4H_2O$ (*32*); the central oxygen atoms of these groups form, respectively, two and three short H-bonds to other oxygen atoms at distances of 2.47 to 2.59 angstroms. It is not known whether these short bonds are actually symmetric, but symmetric or nearly symmetric bonds of length as great as 2.54 angstroms have been identified in other substances (*33*). It is thus reasonable to see in these aquo ions a progression toward the bonding environment of oxygen in the hexagonal networks of the proposed "anomalous water" structures. Certainly there must be detailed differences between the electronic structure of oxygen in these ions and in a completely symmetrically H-bonded H_2O phase, because of the net charge of the ions, the different electron densities for orbitals occupied by unshared pairs as opposed to bonding pairs, the presence of three as opposed to four hydrogens closely coordinating each oxygen, and the effect of more distant interactions beyond the nearby hydrogen atoms. Nevertheless, oxygen has the same basic electron orbital requirements to accommodate three single O–H bonds plus an unshared pair, in H_3O^+, as to accommodate four half bonds to hydrogen (resonance hybrids of a valence bond and an unshared pair) in a symmetrically H-bonded H_2O structure. A similar situation holds for the collection of full O–H bonds, half bonds, and unshared pairs in the $H_5O_2^+$ and higher aquo ions.

The bonding requirements in H_3O^+ appear to favor sp^2 hybridization of the oxygen bond orbitals, which would leave the remaining p_z orbital for the unshared electron pair. The resulting planar conformation is also favored by the repulsive interactions (both electrostatic and overlap) between the hydrogen atoms. In spite of this, the actual conformation is pyramidal, with an H–O–H angle of 110° to 117° (*49*). In $H_5O_2^+$ and the higher aquo ions, the bonding requirements again favor sp^2 hybridization, and the more so if π bonding between oxygen and bridging hydrogen is possible. Nevertheless, of the 13 crystallographically distinct, 3-coordinated oxygen atoms of these groups in structures so far analyzed (*29–32*), only one, in $HCl \cdot 2H_2O$ (*31*), has a coordination that is approximately planar, the other 12 being markedly pyramidal. These examples show that even in bonding situations appropriate to planar sp^2 bond orbital hybridization of oxygen, there is actually a pronounced tendency to tetrahedral (sp^3) hybridization and the correspondingly nonplanar conformation. The same tendency is also seen, of course, in the conformation of the isolated water molecule, with an H–O–H angle of 104.5°, much closer to the tetrahedral angle (109.5°) than to 120° (sp^2 hybridization) or 90° (p^2). In the theoretical discussions of "anomalous water" structures (*8–12*), no additional factors that should alter the tendency to tetrahedral hybridization have been identified on the basis of the assumed symmetric H-bonding.

These considerations indicate that a single hexagonal sheet of 3-coordinated, symmetrically H-bonded oxygens, like that proposed by Lippincott *et al.* (*8*) and Messmer (*9*), should be puckered rather than planar. When the oxygens are 4-coordinated, as in the multiple-sheet structures of Allen and Kollman (*12*), sp^3 hybridization is even more strongly favored, and the puckering of the sheets should be that appropriate for tetrahedral coordination, as proposed by Linnett (*5*). With this type of hybridization, which makes the four bonds from each oxygen equivalent, the inter- and intrasheet bond lengths should be equal.

On this basis, the greater stability for the planar conformation indicated by quantum mechanical calculations (*12*) either reflects inaccuracies in the method of calculation or else shows that in the "naphthalene-like" molecular grouping chosen for consideration the assumed preponderance of 3-coordination for oxygen (pointed out earlier) causes the equilibrium conformation to be more nearly planar than puckered at the tetrahedral angle. By contrast, calculations for a "benzene-like" hexamer (*12*, table 3A), in which the oxygens and bridging hydrogens were constrained to lie in a planar hexagon, showed greater stability when the external (nonbridging) hydrogens were placed at 109.5° with respect to the bridging hydrogens than when they were placed in the plane, at 120°. Here the quantum mechanical result agrees with the foregoing discussion in favoring a nearly tetrahedral coordination geometry. [Results for a puckered hexamer, with completely tetrahedral geometry, are not given in reference (*12*).] There is no apparent reason why the addition of a second ring, to form a "naphthalene-like" group, should change the stable proton configuration from tetrahedral to planar. This seeming inconsistency in the quantum mechanical results may reflect errors in the method of calculation that do not compensate when different molecular conformations are compared.

Although the 3 + 1 coordination of oxygen proposed by Allen and Kollman (*12*) is not known to occur, approximately planar 3-coordination of H_2O is fairly common (*35*, p. 205; *50, 51*) and there are rare examples of approximately trigonal bipyramidal, 3 + 2 coordination (*35*, p. 207). However, in these examples the water molecules do not form any symmetric hydrogen bonds (*52*), so that these examples are not closely comparable to either the symmetrically H-bonded planar 3-coordination discussed in references (*8–11*) or the 3 + 1 coordination proposed by Allen and Kollman (*12*). In many examples of 3-coordinated H_2O, the third ligand is a metal cation, but planar or approximately planar arrangements of three asymmetric $O\text{–}H \cdots O$ bonds around an H_2O molecule are also known (*53*). This type of coordination, in which the cation or the third, more distant proton is located approximately along the twofold symmetry axis of the molecule on its negative side, probably does not involve significant rehybridization of the water oxygen toward an sp^2 bonding configuration, because this would cause the H–O–H angle to increase beyond the 109° ± 4° found in crystalline hydrates (*35*, p. 212; *54*). Instead, the 3-coordination probably reflects the electrostatic nature of the asymmetric H-bonding interaction (*13*, p. 451; *55*) coupled with the fact that the maximum electron density on the negative side of the water molecule occurs along the twofold axis rather than in the neighborhood of the tetrahedrally directed unshared pairs (*56*). Nevertheless, tetrahedral coordination of H_2O is much more common than planar 3-coordination (*16, 26, 51*), and appears to be achieved whenever composition and other structural constraints allow a sufficient number of protons or other ions to be available for the purpose. The electrostatic control exerted by the unshared pairs on the coordination geometry in this case results from the ridge of high electron density that extends from the region of one lone pair to the other on the negative side of the molecule (*56, 57*). It is to be expected that in symmetric H-bonding, which involves an important covalent contribution, the tetrahedral directionality of the bond orbitals will have an even more definite effect on the coordination geometry.

Analogy with Graphite

According to Allen and Kollman (*12*, p. 1453), "The structure of anomalous water is related to that of ice Ic as graphite is related to diamond." The basis for this proposal appears to be that quantum mechanical computations show the between-sheet bonds to be weaker and about 15 percent longer than the in-plane bonds (*12*, p. 1446). The computations reported (*12*, tables 3, 4, 8; figures 2, 4) give between-sheet bond lengths and energies only for planar sheets, not for puckered sheets, which introduces an a priori bias toward longer between-sheet bonds, because the repulsive interactions between planar sheets are clearly greater than between puckered sheets. For planar sheets, the calculated between-sheet bond lengths (*12*, table 4) are only 0.05 to 0.08 angstrom longer than the in-plane bond length of 2.32 angstroms, an increase of only about 3 percent. Nevertheless, Allen and Kollman (*12*, pp. 1445–1446) predict a between-sheet bond length of 2.6 angstroms, on the basis that "the CNDO/2 method frequently leads to underestimation of internuclear separations by as much as 10 percent—particularly for longer bond distances." This statement does not, however, provide a clear basis for increasing a calculated 2.38-angstrom bond length to 2.6 angstroms, while leaving a 2.32-angstrom bond length unaltered.

If graphite were a close analog of the planar H_2O structure, the between-sheet O · · · O distances would be ~ 2 angstroms longer than the in-plane bonds (*13*, p. 235). Also, the O–H bonds would have a bond number greater by a factor of 4/3 than that in the corresponding diamond-like structure. This increase in bond number for the planar sheets was, in fact, proposed by Lippincott *et al.* (*8*) and Messmer (*9*) on the basis of π bonding, but it is not reasonable, as discussed above.

The appropriate diamond analog is the symmetrically bonded structure of Linnett (*5*), not ice Ic, which, owing to the bond asymmetry, has a very different valence-bond arrangement and has O · · · O bond distances ~ 0.45 angstrom longer than in the proposed planar sheets. If the diamond-graphite analogy were valid, the O–H–O bonds would be only $2 \times 0.08 = 0.16$ angstrom longer in the tetrahedral structure than in the planar structure.

In graphite there is no feature analogous to the between-sheet H-bonding in the structures of Allen and Kollman (*12*). The graphite sheets are held together by weak, nondirectional van der Waals forces, quite unlike the forces expected for H-bonds of length ~ 2.6 angstroms. Because of the weak bonding and consequent large spacing between the sheets, graphite is a low-density polymorph, whereas diamond, in spite of its open, tetrahedral structure, is the relatively high-density phase, stabilized relative to graphite only at high pressure (*58*). This situation is just opposite to what is implied by the proposed analogy with ice Ic and the "anomalous water" structures.

The stacking sequences of hexagonal sheets in the structures of Allen and Kollman (*12*), which are controlled by the H-bonds between the sheets, are different from the stacking sequence in graphite (*13*, p. 234; *59*), in which no corresponding intersheet bonding constraint operates.

In conclusion, there is no good basis for drawing a close analogy between graphite and the proposed planar sheet structures for "anomalous water."

Energy Barrier between Asymmetric and Symmetric H-Bonds

The crucial point in any theory that succeeds in making "anomalous water" plausible in the face of the known properties and phase relations in the H_2O system is the proposal of a high energy barrier to the formation of the "anomalous" structure. Such a barrier would allow ordinary water and a strongly bonded water polymer to coexist in variable proportions, out of equilibrium, which is a prerequisite for a thermodynamically valid explanation of the properties of "anomalous water" in terms of a pseudo-binary system.

Several authors (see *5, 6, 8, 12*) advocate a high energy barrier for interconversion of structures based on symmetric and asymmetric H-bonds. This might seem a safe conjecture in the absence of any well-established H_2O phase with a symmetrically bonded structure, which could provide an experimental test. However, it is possible to estimate the energy barrier between ice and the symmetrically bonded structures of Linnett (*5*). Moreover, it is reasonable to infer that in going from the latter structures to structures A and B of Allen and Kollman (*12*), there is no additional barrier, beyond the energy increase required by the greater instability of the planar-sheet structures, as expected on the basis of the preceding discussion. Thus an estimate of the energy barrier between ice and the structures of Linnett (*5*) sets an upper limit for an important group of the symmetrically H-bonded structures proposed for "anomalous water."

The lack of any additional barrier follows from the fact that structures A and B (*12*) are convertible into the tetrahedral structures of Linnett (*5*) by a displacive transformation, without the breakage of any bonds. The energy barriers for such transformations, which involve only bond bending, are typically very low—so low that the transformations cannot be quenched (*60*). If the analogy with diamond and graphite were valid, one could argue for a high energy barrier on the basis of the known barrier between the diamond and graphite structures (*61*). However, the conversion of diamond to graphite requires, first, the breaking of all bonds between the puckered hexagonal sheets, and, second, the shifting of every second sheet by 1.42 angstroms laterally with respect to the sheets above and below. These considerable disruptions make the diamond-graphite transformation reconstructive (*60*) and account for the existence of a sizable energy barrier. They are made necessary by structural features that cause graphite to be nonanalogous with structures A and B (*12*).

The energy barrier between ice I and structure A, or between ice Ic and structure B, can be evaluated by considering the hydrostatic compression that leads from one structure to the other. The energy of compression, expressed as the potential energy per H-bond, is plotted in Fig. 1. Curves I, II, and III are based on three separate sets of assumptions and sources of information. Each curve is constructed in two parts: $U_A(r)$ represents the potential energy for the normal asymmetric H-bond as a function of the oxygen-to-oxygen distance r in the neighborhood of the potential minimum at $r_A = 2.76$ angstroms; $U_S(r)$ is the energy of a bond constrained to be symmetric at all oxygen-to-oxygen distances, and with an energy minimum assumed to lie at $r_S = 2.32$ angstroms, and 1.0 kilocalorie per mole above the minimum of $U_A(r)$. The $U_S(r)$ curves are thus plotted on the assumption that a metastable symmetric bond of length $r_S = 2.32$ angstroms exists and has a bond energy 1.0 kilocalorie per mole less than the normal asymmetric H-bond. In the region of transition from the asymmetric to the symmetric bond, a composite energy curve is drawn to connect smoothly between $U_A(r)$ and $U_S(r)$ without rising above either curve.

The sources of information for the

individual curves in Fig. 1 are given in (*62–66*). The assumptions made in constructing curve II are such that this curve is probably a maximum estimate of the energy increase on compression. Curve III is purely theoretical (*66*), without any constraint from experimental information on the shape of the potential function near $r = r_A$. It is clear from Fig. 1 that curve III does not represent well the shape of the potential function in this region; hence curve II is preferred.

Curve II (Fig. 1) shows that at equilibrium the energy barrier between the asymmetric and symmetric bonds can be at most about 1.5 kilocalories per mole. (If curve III is admitted, the barrier is about 3.5 kilocalories per mole.) This result is based on the assumed destabilization energy of 1.0 kilocalorie per mole for the symmetric bond, which is an arbitrary value, but consistent with the discussion of bond energy given later. A somewhat lower barrier would result if the symmetric bond were less stable. Beyond a destabilization energy of 4 kilocalories per mole, there would probably be no minimum in the potential energy curve near $r = 2.3$ angstroms, according to Fig. 1, and hence no possibility of the symmetrically bonded structure existing, even metastably, at atmospheric pressure.

If the activation energy for transformation to a symmetrically H-bonded structure is ~ 2 kilocalories per mole, the expected transformation rate at temperatures near 0°C would be rapid. According to standard reaction-rate theory, an activation energy of some 20 kilocalories per mole would be needed to prevent transformation at an appreciable rate (*67*). The energy barrier indicated in Fig. 1 can be equated with the activation energy for transformation if the calculated potential energy curve is valid not only for the crystalline aggregate of H-bonds, from whose properties it was derived, but also for the individual H-bonds independently. If a similar potential energy curve were valid for the H-bonds in other geometrical configurations, such as in structure C of Allen and Kollman (*12*) and the structures of references (*6–11*), it would similarly follow that the energy barrier is inadequate to prevent rapid transformation between asymmetric and symmetric structures of these types.

To avoid this conclusion, it is possible to appeal to cooperative character in the H-bonding, such that the potential energy curve of Fig. 1 is valid only for a substantial aggregate of molecules, the potential minimum near $r =$ 2.3 angstroms disappearing for smaller aggregates. Such an appeal was made by Linnett (*5*, p. 1720), but without an assessment of the magnitude of the cooperative effect, and without an explanation of its basis. Quantitative support for a cooperative effect is given by the reported quantum mechanical calculation of an energy increase of 75 kilocalories per mole upon removal of one water molecule from a symmetrically bonded planar ring hexamer, leaving a noncyclic pentamer (*12*, p. 1451). This result implies that, upon breakage of two bonds, the remaining four bonds in the pentamer are each destabilized by ~ 14 kilocalories per mole, ending up with an antibonding energy of ~ 5 kilocalories per mole. By comparison with asymmetric H-bonds, for which a cooperative bond energy stabilization of ~ 1 kilocalorie per mole in aggregates is known (*13*, pp. 459, 461; *68*), the predicted 14 kilocalories per mole for symmetric H-bonding appears extreme.

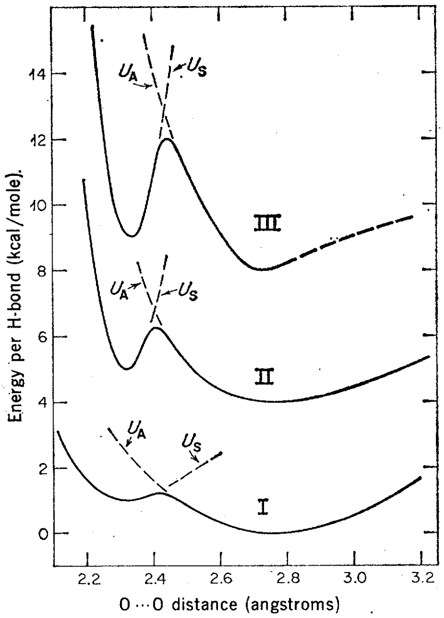

Fig. 1. Potential energy curves for the hydrogen bond in the neighborhood of the potential minimum, constructed on the assumption that a symmetric bond of length 2.32 angstroms exists and is 1.0 kilocalorie per mole less stable than the normal asymmetric bond. For clarity, cuves II and III are displaced upward by 4 and 8 kilocalories per mole, respectively. See the text for assumptions and sources of information used in constructing the different curves.

It is possible that this extreme effect could be the result of errors arising in the quantum mechanical method of calculation. If the potential energy contribution $U_S(r)$ in Fig. 1, which stabilizes the assumed symmetric bond of length 2.32 angstroms, were to disappear altogether when one molecule is removed from a ring hexamer while the remaining molecules are held fixed, one could reasonably expect that the energy of the remaining bonds would not be more than $U_A(r)$ at $r = 2.32$ angstroms. On this basis, the bonds would be destabilized by no more than 1.5 kilocalories per mole (Fig. 1, curve I) or 4.5 kilocalories per mole (curve II), much less than the calculated 14 kilocalories per mole (*12*). These estimates depend on the form of the potential curves, $U_A(r)$, derived for the ice structure, but it is unlikely that curves for other reasonable asymmetric bonding geometries, such as planar 3-coordination, would differ greatly.

If the assumed cooperative effects are greatly reduced in the pentamer, so that the curve $U_S(r)$ is raised to near or above $U_A(r)$, then there will no longer be a potential minimum near $r = 2.32$ angstroms, and the bonds in the pentamer will be free to expand toward the asymmetric H-bond minimum near $r = 2.76$ angstroms. In this case the energy increase calculated upon removing one molecule from the hexamer while keeping the other molecules fixed will not represent the minimum energy barrier for the reaction

$$\text{hexamer} \rightarrow \text{pentamer} + \text{monomer}$$

To find the minimum (saddle point), the energy of the system must be followed as a function of coordinates describing both the withdrawal of the one molecule and also the bond length and symmetry of the remaining bonds in the pentamer. Since this is not done in reference (*12*), one cannot take the calculated energy increase of 75 kilocalories per mole, even if it is numerically valid, as the energy barrier for the dissociation reaction.

Allen and Kollman (*12*, footnote 35) argue that, after breakage of an anomalous-water bond, the remaining bonds will not become asymmetric "because of the between-layer interconnections." This reasoning seems to imply that the between-layer bonds will force the oxygen atoms of a broken ring to stay at the symmetric bond distance of 2.3 angstroms, in spite of the large instability (calculated as ~ 15 kilocalories per mole) relative to asymmetric bonds of length ~ 2.8 angstroms. There are two reasons for not accepting

Table 2. Minimum energy E_m of an "anomalous" H_2O phase of density 1.6 grams per cubic centimeter, deduced from the energies of the known ice phases. The molar volume difference ΔV between each ice phase and the "anomalous" phase is based on a density for the latter that is increased from 1.60 grams per cubic centimeter by an amount required by the compressibility that corresponds to $U_s(r)$ in Fig. 1, curve II. The assumed entropy difference ΔS includes only the configurational entropy of proton disorder, 0.81 entropy unit. The E_m values are $E_m = E - P\ \Delta V + T\ \Delta S + \Delta E_d$, where the (small) decompression energy change ΔE_d for the "anomalous" phase is calculated by the method of reference (*48*), on the basis of the potential function $U_s(r)$ in Fig. 1, curve II.

Ice	E (kcal/mole)	ρ (g/cm^3)	P (kb)	T (°K)	$-P\ \Delta V$ (kcal/mole)	$T\ \Delta S$ (kcal/mole)	E_m (kcal/mole)
I	0.01	0.92	2	250	0.38	−0.20	0.18
II	.02	1.18	4	235	.38	.00	.40
V	.36	1.27	6	260	.43	− .21	.58
VI	.46	1.36	12	300	.57	− .24	.79
VIII	.89	1.58	25	270	.25	.00	1.18

this argument: (i) breakage of a ring occurs at the exterior surface of the structure, where between-layer bonding will generally be incomplete; and (ii) resistance to elongation of the bonds in the broken ring is provided by bending of the between-layer bonds, and the force constant for bending is much less than for elongation (*69*).

An upper limit on the energy barrier for the transformation

symmetric → asymmetric hexamer

can be set by considering a uniform expansion of the ring. In this expansion there is no possibility of an energy increase due to loss of cooperative effects in the sense discussed above. Since the bond energy calculated for the hexamer (*12*, table 3A) is comparable to that taken as appropriate to "anomalous water" (*12*, p. 1446), it is reasonable to assume that the potential curves of Fig. 1 are applicable. The energy barrier is then $6 \times 0.5 = 3$ kilocalories per mole (curve I), or $6 \times 1.5 = 9$ kilocalories per mole (curve II). These barriers are too low to prevent the transformation. A barrier of about 18 kilocalories per mole is indicated by the dubious curve III; although still much less than the barrier of 75 kilocalories per mole of reference (*12*), it is large enough that the quantitative validity of curve II as an upper limit to the bond compression energy is important to the reasoning here.

The short H-bonds observed in $H_5O_2^+$ and the higher aquo hydrogen ions (*29–32*) are direct evidence that a prohibitively high energy barrier does not intervene to prevent small groups of water molecules from forming symmetric H-bonds. In these ions electrostatic interaction of the extra protonic charge with the H_2O dipoles provides a strong contractive force on the O–H–O bonds, which results in the stabilization of some of the bonds in a symmetric or nearly symmetric configuration. Because of the effect of the net charge, these ions do not give a direct indication of the possibility of a stable symmetric bond between neutral water molecules. One example of a very short (2.38 angstroms) H-bond between two water molecules has been reported, in a crystalline hydrate (*70*). However, except for this example and for short intramolecular H-bonds (*31*), the reported instances of symmetric or nearly symmetric O–H–O bonds invariably involve charged molecular groups, either ionic dimers (*35*, p. 182), or, in one instance, ionic chains of infinite length (*71*). Most of these groups are anionic, but there is one example (*13*, p. 485) of a cationic dimer [acetamide hemihydrochloride, containing the cation $(NH_2CH_3CO)_2$-H^+], which is analogous to the aquo hydrogen ions in that the cationic charge is conferred by the extra proton. Although the role of ionic charge is evidently important in the formation of stable symmetric H-bonds, their existence in the aquo hydrogen ions gives cause to doubt the great instability calculated in reference (*12*) for small noncyclic groups of water molecules joined by such bonds.

Even if the reasoning that leads to the potential energy curves in Fig. 1 were faulty, and a much higher energy barrier were to intervene between the asymmetric H-bond and a possible stable symmetric bond of length 2.3 angstroms between neutral molecules, the existence of $H_5O_2^+$ as a stable ion provides an activation mechanism that circumvents the need to pass over the supposed high energy barrier in forming the symmetric bond. The well-known ion states in liquid and solid H_2O are normally considered to be H_3O^+ and OH^-, and are present in concentrations sufficient to allow rate phenomena dependent on them to proceed with appreciable rates at ordinary temperatures. The $H_5O_2^+$ dimer, linked by a short H-bond, is energetically stable relative to $H_3O^+ + H_2O$ in the condensed H_2O phases (*72*) as well as in vapor (*73*), and its existence in known substances (*29–31*) shows that there is no energy barrier high enough to prevent its formation. Consequently, it is reasonable to expect that the propagation of such ion-dimer states through an asymmetrically bonded H_2O structure will serve as an activation complex to promote transformation to a symmetrically bonded structure, if the latter is thermodynamically stable.

On the basis of this idea, an attempt has been made to synthesize "polywater" by a corona discharge in moist air (*74*), in which the principal charge carriers are the aquo hydrogen ions. The experiment was unsuccessful, producing a nitric acid solution rather than "polywater" (*75*). This failure can be considered evidence that the "polywater" structure is not stable under the pressure and temperature conditions of the gas discharge.

Stability

The original proposal (*1*), that "anomalous water" is the stable H_2O phase under ordinary conditions, and that ordinary water is metastable with respect to it, was reinforced by the conclusion that the H-bond energy in "polywater" is 30 to 50 kilocalories per mole (*8*), much greater than the asymmetric H-bond energy of 5 kilocalories per mole (*13*, p. 468). This conclusion was based on the proposal of a symmetrically bonded structure and its analogy with the bonding in HF_2^-. Although one quantum mechanical calculation for a symmetrically bonded ring hexamer (*9*) gave bond energies comparable to those advocated by Lippincott *et al.* (*8*), other such calculations for a variety of planar sheet structures with symmetric bonds indicated a bond stability comparable to or somewhat less than that of asymmetrically bonded structures (*11, 12*). Pedersen (*10*) found from similar calculations for symmetrically bonded planar systems that positively charged, noncyclic polymers should have stronger bonds than neutral single rings or than negatively charged multiple rings such as those proposed by Lippincott *et al.* (*8*); this result is in harmony with the observation that symmetric bonds occur in the aquo hydrogen ions, but not between neutral H_2O molecules, with the one possible exception noted earlier (*70*). However, Pedersen's results (*10*) were given in terms of calculated bond numbers rather than energies.

In all the quantum mechanical treatments (*9–12*), the same basic method of calculation was used (*76*). The calculations of Allen and Kollman (*12*) are the most extensive and thorough, and provide the best theoretical basis for judging the stability of the proposed symmetrically bonded structures. It is, of course, widely recognized that the relative stabilities of different structural conformations obtained quantum mechanically by taking the difference between large calculated energy values are usually subject to large percentage errors, of uncertain magnitude, but larger for more complex systems. References (*9–12*) contain abundant warnings to this effect. Allen and Kollman (*12*, p. 1444) take, however, a more positive position, and argue that for neutral molecular species, the calculated relative energies can be relied upon. In fact, they conclude (*12*, p. 1453) that the quantum mechanical calculations, and arguments based on them, establish the existence of "anomalous water" (*76a*). However, in the previous discussion I cite two instances in which the calculated energy comparisons between symmetrically bonded structures differ by several kilocalories per mole from what is expected on independent grounds (*77*). In assessing the stability of "polywater" relative to ordinary water, the energy comparison is between electronic configurations that differ much more than in a comparison between different conformations of symmetrically bonded structures alone; hence the uncertainty in the energy comparison should be greater. The discrepancy between the calculated asymmetric O–H · · · O bond energy of 8.3 to 10.8 kilocalories per mole (*12*) and the observed value of 5 kilocalories per mole (*13*, p. 468) would suggest that the method (*12*) gives errors of several kilocalories per mole, unless it could be shown by calculations on known systems, both asymmetrically and symmetrically bonded, and of complexity comparable to the unknown systems considered, that this discrepancy is a constant systematic error and disappears in comparisons between such systems.

A more accurate lower limit on the energy of an "anomalous" structure can be established experimentally by comparison with known H_2O phases, provided one accepts the conclusion of the previous section that an energy barrier sufficient to prevent the formation of the "anomalous" structure does not exist. Table 2 gives such a comparison for a structure of density 1.6 grams per cubic centimeter, as assumed by Allen and Kollman (*12*). Since the contemplated "anomalous" structures in reference (*12*) are crystalline (or "microcrystalline"), the proper comparison is with the known solid phases. A comparison with the liquid phase would be appropriate if something reliable could be said about the fusion energy of the contemplated structures, but this poses many difficulties; even for ordinary water, the fusion energy is not well understood (*16*). Listed in Table 2 are the internal energies (at the pressure P and temperature T given) of several of the forms of H_2O, relative to ice I, which serves as the standard of energy for normal, asymmetric H-bonds. [Allen and Kollman (*12*) use liquid water as the energy reference, but this is less appropriate, because the nature of the hydrogen bonding is less well understood in liquid water than in ice I (*16*), and because of the lack of information on the fusion energy of the "anomalous" structures.] Also listed in Table 2 are the free energy contributions $-P\,\Delta V$ and $T\,\Delta S$ by which a phase of density 1.6 grams per cubic centimeter (at $P = 0$) and zero proton configurational entropy (appropriate to symmetric H-bonds) would tend to be stabilized at the indicated P and T, relative to the known phases. The quantity E_m in Table 2 is the energy (after decompression to atmospheric pressure) that the "anomalous" structure would need to have if it were in equilibrium with the known phases at P, T. The density of the anomalous structure under pressure, and the energy change on decompression, are calculated by the method of Kamb (*48*, section 2), with the assumption that the compressibility and thermal expansion of this structure are appropriate to the potential energy function $U_S(r)$ given in Fig. 1 (curve II). On the basis of the discussion in reference (*48*), the E_m values in Table 2 are probably reliable to ±0.2 kilocalorie per mole. If, as argued above, none of the phases in Table 2 can be metastable with respect to the "anomalous" structure, the values E_m are minimum values for the energy of this structure.

It follows that symmetric H-bonds of the type proposed for "anomalous water" (*12*) have an energy at least 0.6 kilocalorie per mole greater than normal, asymmetric H-bonds (*78*).

Catalysis

If the "anomalous water" structure were energetically stable relative to ordinary water, as argued in references (*1*) and (*8*), and if there were a high energy barrier for transformation from the asymmetrically bonded to the symmetrically bonded structures, then it would be possible to appeal to catalysis as a mechanism for allowing "anomalous water" to form. The proposed catalytic action is attributed to a silica or glass surface (*79*).

By contrast, Allen and Kollman (*12*, p. 1449) propose catalysis as a mechanism for forming an "anomalous water" structure under conditions when this structure is thermodynamically unstable relative to normal water. This proposal conflicts with the established nature of catalysis. Catalysis alters the rate of a chemical reaction without changing its equilibrium. When the catalyst is present in high concentration, the equilibrium of the reaction can be affected, but in this case the reaction is taking place in the medium provided by the catalyst, and the equilibrated reactants and products remain in this medium and continue to interact energetically with it (*80*). It is reasonable for Allen and Kollman (*12*, p. 1450) to postulate that the equilibrium is shifted in the direction of the symmetrically H-bonded structure in a layer 10 to 15 angstroms thick adsorbed on a silica or glass surface and interacting energetically with it. But it is not reasonable to propose that the symmetrically bonded molecular groups that escape from the adsorbed layer into the external (nonadsorbed) region, where they do not interact with the catalyzing surface, build up there a concentration greater than would be allowed by the equilibrium between asymmetrically and symmetrically bonded structures in the absence of the catalyst (*12*, p. 1450). There is no thermodynamic validity to the proposition (*12*, p. 1451) that the concentration of "anomalous" molecular groups (*81*) will build up in the nonadsorbed medium until the average free energy of the material (adsorbed plus nonadsorbed) in the capillary is the same as that of normal water. For a macroscopic system consisting of two separate phase regions (adsorbed and nonadsorbed), the average free energy is of no significance. The pertinent free energy quantities are the partial molar free energies of the "anomalous" molecular species in the two phase regions; at equilibrium these free energies are equal, but this equality does not affect the equilibrium concentration in the nonadsorbed phase (*82*).

Conclusion

In the discussion of "anomalous water," structural theorizing has been directed toward making the properties of this material credible under the assumption that it is a pure H_2O phase. This credibility is an important part of the effort to establish the existence of such a phase, because many of its reported properties are "anomalous" in the sense that, as properties of pure H_2O, they appear to conflict with principles of physical chemistry and with what is known about ordinary water. Because the existence of the "anomalous" phase would have far-reaching implications, it is important not only to test its experimental basis independently, but also to examine the theoretical explanations for consistency with structural principles and with available evidence on the forces of interaction between water molecules. From this point of view, many of the proposed structural models have unsatisfactory features. One symmetrically H-bonded model emerges that is satisfactory in terms of known stereochemistry and that would probably provide a reasonable basis for the "anomalous" phase, except that the possible energy barrier for conversion of the proposed symmetric H-bonds to ordinary asymmetric H-bonds is demonstrably too low to prevent transformation of the proposed structure to ordinary water. A similar difficulty is found for models based on asymmetric H-bonds. Thus, if constraints imposed by known stereochemistry are accepted as the basis for judgment, no adequate structural basis for "anomalous water" has been advanced. This conclusion reinforces recently expressed doubts about the experimental validity of "anomalous water," and it emphasizes the significant changes in H-bond stereochemical concepts that would be required in the unlikely event that structures of the type proposed to explain "anomalous water" were to be verified experimentally.

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35. W. C. Hamilton and J. A. Ibers, *Hydrogen Bonding in Solids* (Benjamin, New York, 1968).

36. G. E. Bacon and N. A. Curry, *Acta Crystallogr.* **9**, 82 (1956).

37. Each of the remaining six oxygen atoms forms bonds to neighbors that lie at the four basal corners of a rectangular pyramid, relative to the original oxygen at the vertex. The vertex angle is 60°, and accordingly there are four O · · · O · · · O bond angles of 60° for each such oxygen atom, in addition to two angles of 109.5°. Such one-sided 4-coordination, with such small bond angles, is far from anything that occurs in any known H_2O phase or hydrate. Donohue (*6*) omitted the 60° bond angles in his description of the structure. For symmetrical O–H–O bonds there is no geometrical difference between the two "canonical forms" shown (*6*, figure 1) for the rhombic dodecahedral unit, and all of the O · · · O · · · O angles about each oxygen atom are equally significant. Even for asymmetric H-bonds, for which the "canonical forms" are distinguishable as shown, and for which the donor O · · · O · · · O angles are satisfactory, the acceptor relation involving the 60° angles is quite unsatisfactory. In none of the ice phases does a distortion from tetrahedral bonding coordination occur that is even remotely as great.

38. M. Ageno [*Theor. Chim. Acta* **17**, 334 (1970)] has proposed a similar model both for "anomalous water" and for ordinary water.

→ B. Kamb and B. L. Davis, *Proc. Nat. Acad. Sci. U.S.* **52**, 1433 (1964).

40. B. Kamb, in *Collected Abstracts, 8th International Congress of Crystallography* (International Union of Crystallography, Stony Brook, N.Y., 1969), p. S117.

41. The required pressure is 49 kilobars if the dashed part, labeled U_A, of curve I in Fig. 1 is applicable and if the symmetric bond length is 2.40 angstroms. If the solid part of curve I (Fig. 1) is applicable, the pressure is 7 kilobars. The transformations of ice I to ices II and III take place at about 2 kilobars.

42. The term "bond order" used without specific definition in (*8*) is here replaced by the essentially equivalent term "bond number" in the sense defined by Pauling (*13*, p. 255).
43. If the $2p_z$ orbital of hydrogen could be used for π bonding, then the $2p_x$ orbital could equally well be used to form an *sp* hybrid that would accommodate the electron pairs of full O–H bonds (bond number, 1) in the linear O–H–O bond configuration. This formation of a hybrid bond should cause the bonds to shorten to the full-bond length, which probably is about 1.0 angstrom (O···O distance, 2.0 angstroms), although an experimentally based value cannot be given since this type of bonding has never been found. The O–H bond number in the planar structure, including the π contribution, would be 4/3, and in the tetrahedral structure, 1. The relative stabilities of the two structures would be unaffected by this alteration from the bond numbers given in (*8*).
44. The possibility of significant π bonding with the use of the 2*p* orbital of hydrogen has been denied also by A. Azman, J. Koller and D. Hadzi [*Chem. Phys. Lett.* **5**, 157 (1970)].
45. In the title of a discussion supplementary to (*12*), L. C. Allen and P. A. Kollman *J. Amer. Chem. Soc.* **92**, 4108 (1970)] refer to the bonding as that of "divalent hydrogen," without clarification in the text as to this meaning of the term "divalent." According to conventional concepts of chemical bonding, divalency could be achieved only with use of the 2*s* or 2*p* orbitals of hydrogen, which, however, is discounted in (*12*). The O–H bond lengths for symmetrical H-bonds indicate that the H atoms are monovalent (*13*, p. 484).
46. In a discussion supplementary to (*12*), L. C. Allen [*Nature* **227**, 372 (1970)] introduces a sheet-stacking sequence that is said to be different from those in (*12*), but which is, in fact, the same as in structure B of (*12*), analogous to ice Ic. The bonding electron arrangement for this structure is presented in terms similar to those used in (*5*).
47. Figure 4b of (*12*) shows no oxygen atoms as 4-coordinated. In the text (*12*, p. 1447) Allen and Kollman point out that a proton should be added for electrical neutrality, but they do not state whether the energy given in figure 4b was calculated for the molecule as shown or with the extra proton added.
48. B. Kamb, *J. Chem. Phys.* **43**, 3917 (1965).
49. Theoretical calculations (J. A. Pople, personal communication) suggest that the H_3O^+ ion, in isolation, may be planar, and therefore that the nonplanar configuration observed in crystals indicates a significant effect of the H-bonding interactions.
50. L. Bragg, *Crystal Structures of Minerals* (Cornell Univ. Press, Ithaca, N.Y., 1965), p. 361.
51. J. R. Clark, *Rev. Pure Appl. Chem.* **13**, 50 (1963).
52. An exception, noted earlier, is one of the two oxygen atoms of the $H_5O_2^+$ ion in $HCl \cdot 2H_2O$ (*31*).
53. Clark (*51*) gives four examples in which the sum of the three O···O···O angles about the water molecule is greater than 350°.
54. Two examples showing some indication of sp^2 hybridization for H_2O coordinated to transition metal atoms are cited in (*35*, p. 215).
55. W. Baur, *Acta Crystallogr.* **19**, 909 (1965).
56. This result was indicated by the quantum mechanical calculations → J. Lennard-Jones and J. A. Pople, *Proc. Roy. Soc. Ser. A Math. Phys. Sci.* **205**, 155 (1951). In more recent treatments the results have not been presented in a form that makes it possible to check this point.
57. B. Kamb, *Acta Crystallogr.* **17**, 1446 (1964).
58. W. Klement and A. Jayaraman, *Progr. Solid State Chem.* **3**, 325 (1966).
59. This applies to the normal, hexagonal form of graphi → [L. Pauling, *Proc. Nat. Acad. Sci. U.S.* **56**, 1646 (1966)]. The relatively rare rhombohedral form of graphite has topologically the same stacking sequence as diamond or the B structure of (*5*): F. Laves and Y. Baskin, *Z. Kristallogr.* **107**, 337 (1956); A. R. Ubbelhode and F. A. Lewis, *Graphite and Its Crystal Compounds* (Oxford Univ. Press, New York, 1960), p. 2.
60. M. J. Buerger, *Fortschr. Mineral.* **39**, 17 (1961); in *Phase Transformation in Solids*, R. Smoluchowski, J. E. Mayer, W. A. Weyl, Eds. (Wiley, New York, 1951), p. 183.
61. B. J. Alder, in *Solids under Pressure*, W. Paul and D. M. Warschauer, Eds. (McGraw-Hill, New York, 1963), p. 404.
62. For curve I (Fig. 1) $U_A(r)$ is represented by the cubic polynomial derived by Kamb (*48*, equation 2). A similar cubic polynomial is used for $U_S(r)$, the coefficient of the quadratic term (189 kilocalories per mole) being obtained from a force constant for bond compression deduced as follows. The OH stretching frequency of 1600 reciprocal centimeters for symmetric O–H–O bonds (see *63*) corresponds to a force constant $k = 0.75 \times 10^5$ dynes per centimeter for the stretching of each of the two O–H bonds separately. The appropriate force constant for compression of the whole O···O bond would be ½ *k*, if the force constants for symmetric and antisymmetric stretching of the O–H–O unit were equal. This equality holds to a fair approximation for triatomic molecules generally; it is shown, for example, in the near equality of the stretching frequencies $\nu_1 = 3657$ reciprocal centimeters and $\nu_3 = 3776$ reciprocal centimeters for H_2O. However, the force constant used in the polynomial for $U_S(r)$ is increased by a factor of 1.3, which is the ratio of the force constants for symmetric and antisymmetric stretching of CO_2, and is the largest such ratio for linear triatomic molecules for which data are available. The coefficient of the cubic term (– 754 kilocalories per mole) is obtained by the method of Kamb (*48*), with the Grüneisen γ taken as 2.0, a value typical of many solids. Because a bond compression from 2.76 to ~2.4 angstroms represents a finite elastic strain, anharmonicity of higher order than the cubic term used in calculating curve I may contribute significantly. The form of $U_A(r)$ for curve II is therefore calculated from the theory of finite strain, on the basis of the following equation of state, which has been found applicable to a variety of crystalline solids up to high pressure P and large compressions V_0/V (see *64*):

$$P = \frac{B_0}{a}\left[\left(\frac{V_0}{V}\right)^a - 1\right]$$

where V_0 is the specific volume and B_0 is the bulk modulus at $P = 0$. The bond compression energy is obtained from this equation by integration with respect to V. Strictly speaking, the compression energy so obtained is the Helmholtz free energy rather than the potential energy of the bonds, but the difference between these two energy quantities is small enough to be disregarded in the present discussion (see *65*). The constant a in this equation is related to the Grüneisen γ (*65*) by

$$\gamma = ½\,(a - ⅓)$$

From the measured thermal expansion of ice I, a should have the value 1.5, according to this equation. However, to set an upper limit on the possible effects of anharmonicity, the value $a = 5.5$ is used in constructing $U_A(r)$ for curve II, the higher a value representing increased anharmonicity and a more steeply rising potential energy as the bonds are compressed. The value $a = 5.5$ is chosen because it fits experimental data over a compression range up to $V_0/V = 1.55$ for NH_4Cl, the substance that is structurally most nearly like ice among the various materials investigated (see *64*), most of which have a values from 4 to 6. To avoid the possibility that the curvature of $U_S(r)$ in curve I is under estimated because of an anomalously flat potential minimum for the proton in the symmetric H-bond, which might lead to a significant difference between the effective force constants for antisymmetric and symmetric stretching of the O–H–O unit, an overestimate is used in drawing $U_S(r)$ for curve II. The curve is drawn as a Morse function with a dissociation energy of 122 kilocalories per mole (the sum of the first dissociation energy for H_2O, 118 kilocalories per mole, and an assumed bond energy of 4 kilocalories per mole for the symmetric H-bond), and with curvature appropriate to individual O–H stretching force constants equal to that in H_2O vapor. This curvature is certainly too large, since in the symmetric H-bond the individual O–H bonds are only half bonds. Curve III is obtained from the H-bond potential functions of Reid (see *66*). Since these functions do not describe any double-minimum potentials of the type contemplated in Fig. 1, in order to use them here two separate functions $U_A(r)$ and $U_S(r)$ must be combined, as in curves I and II. The quantity $U_A(r)$ is the calculated energy for an asymmetric bond of equilibrium length $r_A = 2.74$ angstroms (*66*, figure 3), and $U_S(r)$ is the energy for a bond that is constrained to remain symmetric at all distances (from *66*, figure 4). Actually, the $U_S(r)$ curve was calculated (*66*) on the assumption that the potential minimum is at $r_S = 2.42$ angstroms and lies about 30 kilocalories per mole lower than the minimum for $U_A(r)$; in Fig. 1 this calculated $U_S(r)$ curve has simply been translated to the position shown.
63. R. Blinc, D. Hadzi, A. Novak, *Z. Elektrochem.* **64**, 567 (1960). The frequency, 1600 reciprocal centimeters, agrees with that chosen by Lippincott *et al.* (*8*) as appropriate for a symmetric H-bond.
64. H. G. Drickamer, R. W. Lynch, R. L. Clendenen, E. A. Perez-Albuerne, *Solid State Phys.* **19**, 135 (1966). The equation was proposed by F. D. Murnaghan [*Finite Deformation of an Elastic Solid* (Wiley, New York, 1951), chap. 4]. The relation of this equation to other finite-strain equations of state is discussed by J. J. Gilvarry [*J. Appl. Phys.* **28**, 1253 (1957)].
65. J. J. Gilvarry, *Phys. Rev.* **102**, 331 (1956).
66. C. Reid, *J. Chem. Phys.* **30**, 182 (1959). This paper presents an elaboration of an H-bond potential function introduced by E. R. Lippincott and R. Schroeder [*J. Chem. Phys.* **23**, 1099 (1955)].
67. If the usual pre-exponential factor of 10^{13} per second is applicable in the Arrhenius equation for the appropriate rate constant, an activation energy of 16 kilocalories per mole corresponds to a rate constant of 1 per second at 273°K.
68. This matter has been considered theoretically by J. Del Bene and J. A. Pople [*J. Chem. Phys.* **52**, 4858 (1970)]; for asymmetrically bonded cyclic pentamers and hexamers they calculate a cooperative increase in bond energy of about 4.5 kilocalories per mole, rather larger than the ~ 1 kilocalorie per mole estimated experimentally in (*13*).
69. For the asymmetric H-bonds in ice, the force constant for transverse (bending) displacement of oxygen from the equilibrium bond direction is 0.053 times the force constant for longitudinal (stretching) displacement. This ratio is calculated from information in (*16*, p. 507) and (*48*). For the free water molecule, the force constant for transverse displacement of the H atoms is 0.19 times that for longitudinal (stretching) displacement. For symmetric O–H–O bonds, the situation would probably be intermediate between the foregoing two extremes. If a ratio of 0.1 is assumed, and if the bending of one between-layer bond constrains the elongation of one within-ring bond, the latter bond will elongate to about 2.7 angstroms.
70. B. M. Craven, S. Martinez-Carrera, G. A. Jeffrey, *Acta Crystallogr.* **17**, 891 (1964). The interpretations of the dimer as neutral is not entirely certain, because the proton arrangement in this rather complexly H-bonded structure had to be deduced by indirect, but reasonable, arguments. There is also perhaps some uncertainty, as the authors discuss, that the O···O distance is as short as 2.38 angstroms.
71. G. Ferguson, J. G. Sime, J. C. Speakman, R. Young, *Chem. Commun.* **1968**, 162 (1968).
72. The inferred stability is based on the vapor-phase binding energy of 21.9 kilocalories per mole reported (see *73*) for $(H_2O_5)^+$, corresponding to a binding energy of about 17 kilocalories per mole relative to the asymmetric H-bond in ice. From this energy must be subtracted about 0.23 kilocalorie per mole due to the stretching of the six surrounding H-bonds when the short H-bond contracts in the ice structure; this stretching energy is obtained from Fig. 1.
73. M. De Pas, J. J. Leventhal, L. Friedman, *J. Chem. Phys.* **49**, 5543 (1969).
74. A. G. Leiga, D. W. Vance, A. T. Ward, *Science* **168**, 114 (1970).
75. Leiga *et al.* (*74*) call attention to the significant

fact that the infrared spectrum of the nitric acid solution is very similar to that reported for "polywater" (*8*).

76. The quantum mechanical method used in (*9–12*) is the CNDO/2 method, or its successor INDO. Other calculations by the CNDO or CNDO/2 methods, for similar models of "anomalous water," are reported by Azman *et al.* (*44*) and by A. Goel, A. S. N. Murthy, and C. N. R. Rao [*Chem. Commun.* **1970**, 423 (1970)]. In a recently reported calculation by a somewhat different method (IEHT), no indication of stability for H-bonds shorter than 2.6 angstroms was found in puckered hexamers, planar hexamers, or planar pentamers [A. P. Minton, *Nature* **226**, 151 (1970)]. The reason for this serious discrepancy with the results of (*9–12*) is not clear. It is possible that the shortness of the symmetric bond length (2.32 angstroms) obtained by Allen and Kollman (*12*) results from the tendency of the CNDO/2 method to underestimate bond distances (*12*, p. 1446). Evidence to support this hypothesis is the very short O · · · O distance of 2.53 angstroms calculated for an asymmetrically bonded pentamer (*12*, p. 1446). Allen and Kollman (*12*) do not give calculated energies for structures with intermediate bond asymmetries which would permit one to check whether the symmetric structure is theoretically stable against a distortion toward the asymmetric structure. Such a calculation is crucial to a theoretical discussion of the possible energy barrier for interconversion of symmetric and asymmetric structures.

76a. However, Allen and Kollman have recently concluded from further quantum mechanical calculations that "polywater" does not exist (L. C. Allen and P. A. Kollman, unpublished manuscript kindly supplied by the authors, 1971). The newer, more accurate (*ab initio*) calculations, for cyclic $(H_2O)_6$ hexamers, give a bond energy that is lower by about 5 kilocalories per mole for symmetric bonds than for asymmetric bonds. The more accurate calculations do not consider molecular arrangements as complex as those treated in the earlier work (*12*).

77. Another instance is the calculated energy comparison between structure C and structures A and B (*12*, table 4 and figure 3). In structure C the protons in the between-sheet bonds are only 2.32 angstroms apart, whereas in structures A and B they are 4.02 angstroms apart. This substantial increase in a distance corresponding to an important repulsive energy contribution should cause structures A and B to be substantially more stable than structure C. However, the calculated energies [quantities *E* in the footnotes to table 4 (*12*)] show the molecular group representing structure C (*12*, figure 3a) as more stable by 1.4 to 2.2 kilocalories per mole of H-bonds than the groups representing structures A and B (*12*, figure 3, b and c).

78. The H-bond energy quoted does not include a correction for the greater van der Waals energy due to interactions between nonbonded neighbors in the dense phases This correction could be calculated for an "anomalous" phase if its structure were known in detail.

79. P. W. Bridgman [*Proc. Amer. Acad. Arts Sci.* **47**, 441 (1912)] sometimes incorporated powdered glass in water samples carried to high pressure, for the specific and successful purpose of causing H_2O phases to nucleate, and yet he never obtained a phase attributable to the "anomalous" form of water, even though high pressure should tend to stabilize such a phase. This lack of success reflects either on the assumed mechanism of catalysis or on the stability of "anomalous water."

80. Discussions of these fundamental ideas about catalysis are numerous in the literature; for example, P. G. Ashmore, *Catalysis and Inhibition of Chemical Reactions* (Butterworth, London, 1963), pp. 3–10; S. J. Thomson and G. Webb, *Heterogeneous Catalysis* (Wiley, New York, 1969), p. 1.

81. Confusion is introduced by use of the term "microcrystallites" (*12*, p. 1450) to describe the symmetrically H-bonded molecular grouping visualized as separating from the adsorbed layer and entering the nonadsorbed medium in the capillary. Either these "microcrystallites" are molecular species subject to the laws of chemical mixtures, or else they are crystals that constitute in themselves separate phases. In neither case is the average free energy of the whole system a pertinent quantity. Linnett (*5*, p. 1720) visualizes polywater as containing individual structural units which are called "micelles," and to which a colloidal character is attributed; he does not specify the size of these "micelles," nor does he indicate whether they constitute a separate phase in the thermodynamic sense. Their internal structure, according to the description given (*5*), is that of a crystalline solid.

82. N. K. Adam, *The Physics and Chemistry of Surfaces* (Dover, New York, ed. 3, 1968), pp. 107, 404; A. W. Adamson, *Physical Chemistry of Surfaces* (Interscience, New York, ed. 2, 1967), pp. 78, 414; W. J. Moore, *Physical Chemistry* (Prentice-Hall, Englewood Cliffs, N.J., ed. 3, 1962), p. 737; E. A. Moelwyn-Hughes, *Physical Chemistry* (Pergamon, London, ed. 2, 1961), p. 939.

83. I was encouraged to write this article by discussions with L. Pauling. I acknowledge National Science Foundation support of a program of research on the phases of ice, which provided the background for the present discussion. Contribution No. 1817 from the Division of Geological and Planetary Sciences, California Institute of Technology.

NEWS AND COMMENT

National Research Council: And How It Got That Way

In the last week of April the members of the National Academy of Sciences (NAS) will make their annual migration to Washington. They will spend much of their time in the agreeable ceremonial labors of electing new members to perpetuate their society, bestowing honors, and attending scientific sessions. But this year, on and off the agenda, the members must confront the question of how better to carry out their congressionally chartered responsibilities of providing advisory services to the government.

The NAS meets from 26 April through 29 April, and the National Academy of Engineering (NAE) will follow with its own annual meeting in the Academy's marbled halls on 29 and 30 April. The order and timing of the meetings might be taken as symbolic of the separate but equal status accorded NAE when it was organized in 1964 under the NAS charter. The NAE program will be similar to that of the NAS, but the engineers' mood is likely to be that of an exasperated younger brother who feels his talents and energy are misused in the family business.

A major topic of concern at both meetings will inevitably be the National Research Council (NRC), the operating arm of the NAS and NAE, through which the Academy performs its advisory functions. The NRC has a staff of about 1000 and an operating budget of roughly $30 million this year. NRC performs no laboratory research, of course, but is essentially a vast, *sui generis* committee system drawing on the voluntary services of as many as 9000 American scientists, engineers, and other professionals—which makes it, all in all, the biggest consulting firm in the world.

NAS-NAE-NRC, to use its full, not very brief abbreviation, is replete with paradox. The parent NAS is a unique hybrid, a congressionally chartered, private, nonprofit organization incorporated in the District of Columbia. The government provides no direct subsidy and exercises no oversight authority, but 80 percent of the Academy budget comes from government sources. Perhaps the richest paradox involves the honorary aspects of the Academy. For the individual, membership in the Academy certainly signifies making it in American science. But it is really the NRC which discharges the advisory obligations imposed by the charter. There is nothing in it about the Academy being an honorary society.

Nevertheless, although a minority of Academy members are extensively engaged in NRC activities, it is the prestige of Academy members that gives the organization its unique standing. And, significantly, "Academy" is the generic term commonly used for NAS-NAE-NRC and all its works. If the Academy is not above suspicion or beyond reproach, it remains the court of last resort on scientific and technical questions.*

Since World War II, however, as the

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* Three articles by D. S. Greenberg in *Science* (14, 21, and 28 April 1967) provide extensive background on Academy problems and politics, and, more recently, two articles in the *National Journal* (16 and 30 January 1970) by Claude E. Barfield marshal considerable detail on the operations of NAS-NAE-NRC.