

prising when we consider that the chief processes of interchange are essentially irreversible. Webster, Wahl and Urey [*ibid.*, **3**, 129 (1935)] have found that water made from the oxygen in carbon dioxide is 10.2 p. p. m. heavier than water containing the same hydrogen but with its oxygen isotopes in equilibrium with the carbon dioxide. There can be little doubt that the carbon dioxide of the atmosphere is in equilibrium with the water of the earth. Plants, taking in two atoms of carbon dioxide oxygen and one atom of water oxygen return to the atmosphere a molecule of oxygen and build into plant substance the remaining atom of oxygen. If we assume that there is no discrimination between the isotopes of oxygen in this process, we find that the air oxygen produced by plants should be approximately 6.8 p. p. m. heavy. The small difference between this figure and the value found by Dole may be due either to other slower processes tending toward a state of true equilibrium or to a preferential selection of  $O^{18}$  for the synthesis of plant substance.

We hazard the prediction that water prepared from the oxygen in carbohydrates either will have the same density as water from atmospheric oxygen or will be slightly heavier. Since we do not expect to be able to verify this prediction experimentally for some time we have no desire to reserve the field. We hope that others will be interested in examining the isotopic composition of the oxygen in natural organic substances.

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#### THE STRUCTURES OF ICE AND LIQUID WATER

Sir:

Although the assumption of four "hydrogen bridges" or "hydrogen bonds" connecting each oxygen atom to adjacent oxygens in ice and liquid water accounts satisfactorily for many of their properties, certain properties such as the low conductivity of pure water and the high dielectric constants (for low frequencies) for both solid and liquid near  $0^\circ$  seem to require that these bridges be *unsymmetrical* [Huggins, "Chemistry, the Science of Atoms and Molecules," Preliminary edition, 1933; Bernal and Fowler, *J. Chem. Phys.*, **1**, 515 (1933)]. Pauling's recent calculation [THIS JOURNAL, **57**, 2680 (1935)] of the entropy of ice also favors this conclusion.

Calculations of the change of potential energy of a hydrogen bridge, connecting two like oxygen atoms, as the hydrogen moves along the O-O centerline show in fact *two* minima, if the O-O distance is taken as the experimental value (2.76 Å.) in ice, when one uses for the O-H interaction energy a modified Morse potential function of the form [Huggins, *J. Chem. Phys.*, **3**, 473 (1935); also another article in press]

$$U = e^{-a(r-r_0)} - C'e^{-a'(r-r_0)}$$

obtaining the constants from band spectrum data for the OH molecule.

The minima are about 1.10 Å. from each oxygen. The hump between them is about  $0.15 \times 10^{-12}$  ergs high—enough larger than  $\frac{1}{2} kT$  at ordinary temperatures ( $\sim 0.02 \times 10^{-12}$  ergs) to make jumps of the hydrogen over or through this barrier very rare. One concludes then that the bridges in  $H_2O$  are of the unsymmetrical type, each H nucleus, in effect, bridging between an  $OH^-$  ion and an  $H_2O$  molecule. The potential curve for such a case has but a single minimum, close to the  $OH^-$  end. In other words, two hydrogens of the four surrounding each oxygen are close ( $\sim 1.1$  Å.) and two more distant ( $\sim 1.65$  Å.). A very slight unsymmetrical Coulomb force added to the O-H interactions assumed above suffices to eliminate entirely the central hump.

Although a single hydrogen cannot jump to the other end of its bridge by itself, jumps in unison of all of the hydrogens in a ring are possible. This mechanism accounts for the dielectric behavior quite as well as the less likely assumption of rotation of the  $H_2O$  molecules.

Consideration of the effect of the additional Coulomb forces in the cases of hydrogen and hydroxide ions leads one to conclude that the former are best considered as  $(H_2OHOH_2)^+$  ions with a relatively strong symmetrical bridge in the center while the latter are merely  $OH^-$ . Either can contemporaneously add an  $H_2O$  molecule at one end and lose one at the other, the positive ion doing this more readily than the negative. This affords a chain mechanism satisfactorily accounting for the relative mobilities of these ions as compared with others.

These subjects and others related to them will be discussed in detail elsewhere.

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