

**THE PHOTOCHEMICAL FORMATION OF
ETHYLENE IODIDE IN SOLUTIONS OF
CARBON TETRACHLORIDE**

Sir:

Ethylene iodide, which decomposes photochemically when exposed to the 303 and 313 $m\mu$ mercury lines [THIS JOURNAL, 57, 2411 (1935)] and undergoes an iodine sensitized decomposition at wave lengths of 436 to 579 $m\mu$ [Dickinson and Nies, *ibid.*, 57, 2382 (1935)], has been found to be formed rapidly when solutions of ethylene and iodine in carbon tetrachloride are exposed to red light. A tungsten lamp with a Corning Filter No. 241 having maximum transmission at a wave length of *ca.* 700 $m\mu$ was used. Solutions containing iodine were thoroughly shaken in an all-glass apparatus at 25° under a constant pressure of ethylene. All air was removed from the system by evacuation while the solution was frozen with a carbon dioxide-alcohol mixture. The rate of disappearance of iodine was determined by light absorption. No measurable dark reaction occurred over periods of thirty-six hours. The rate of the reaction was dependent on the pressure of ethylene and fell off with decreasing concentrations of iodine. Since the efficiency of formation of iodine atoms from excited iodine molecules may be small at λ 700 $m\mu$ (although the falling off in this efficiency with increase in wave length is not as great (Dickinson and Nies, *loc. cit.*) as was formerly thought) the observed photoiodination at 700 $m\mu$ may possibly proceed through the action of excited iodine molecules, whereas the photo-decomposition yields iodine atoms and the sensitized decomposition proceeds through the action of iodine atoms. This mechanism may obtain in the photoiodination of butene-1 by incandescent lamps as reported recently by Forbes and Nelson [THIS JOURNAL, 58, 182 (1936)].

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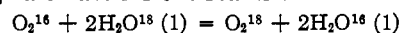
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**AN EXPLANATION OF THE RELATIVELY LARGE
CONCENTRATION OF O¹⁸ IN THE ATMOSPHERE**

Sir:

Dole [THIS JOURNAL, 57, 2731 (1935)] finds in preliminary experiments that water made by combining atmospheric oxygen with hydrogen is 4.6 p. p. m. heavier than water made by combining

oxygen from Lake Michigan water with the same hydrogen. This difference in density Dole (private communication) has since revised to 6.0 p. p. m. Morita and Titani [*Bull. Chem. Soc. Japan*, 11, 36 (1936)] comparing waters made from essentially pure protium report a difference of 8.0 p. p. m. due to the difference between atmospheric oxygen and water oxygen. We have found in this Laboratory differences of 5.8 and 6.2 p. p. m. in two experiments in which we have compared the densities of protium oxide from atmospheric oxygen with protium oxide from water oxygen. Urey and Greiff [THIS JOURNAL, 57, 325 (1935)] calculate for the reaction



an enrichment factor 1.01 at 0°. This corresponds to a water density difference of not more than 2.0 p. p. m. since the enrichment factor diminishes with increasing temperature.

Part of the difference between these figures may be explained if one assumes that the atmosphere is in equilibrium with the ocean in respect to oxygen isotope concentrations. We find that Lake Michigan water is heavier than Cambridge tap water by 0.4 \pm 0.3 p. p. m.—a negligible difference. Gilfillan [*ibid.*, 56, 406 (1934)] reports that ocean water is 2.3 p. p. m. heavier than Cambridge tap water. We have found a difference of 1.8 p. p. m. [*ibid.*, 56, 1650 (1934)]. Thomson, Wirth and Utterbeck's results [*ibid.*, 57, 400 (1935)] indicate that ocean water in general is not more than 1.7 p. p. m. heavier than their fresh water.

Fresh water, being essentially a distillate from the ocean, is presumably lighter because of the greater volatility of water containing the lighter isotopes of hydrogen and oxygen. Although the vapor pressures given by Wahl and Urey [*J. Chem. Phys.*, 3, 411 (1935)] indicate that more than half of the change in density occurring when normal water is evaporated is due to separation of the oxygen isotopes, yet it is improbable that more than 1 p. p. m. of the density difference between ocean water and fresh water is due to the oxygen isotopes.

It seems improbable that either the density measurements of the theoretical calculations are sufficiently in error to account for the remaining difference of 3 p. p. m. The conclusion to which this leads, namely, that the atmosphere is not in equilibrium with the waters of the globe with respect to its content of oxygen isotopes, is less sur-

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° 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]

$$U = e^{-a(r-r_{10})} - C'e^{-a'(r-r_e)}$$

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 0.15×10^{-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 (~ 1.1 Å.) and two more distant (~ 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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