It also follows from the mechanism proposed by Adadurow and Didenko that the (per cent. reaction)-(time) curve for a single experiment must be autocatalytic in nature, since the reaction is assumed to be proceeding on zinc oxide formed by the decomposition of the reactant. No such effect was found, as is shown by Figure 1 of our paper.

It appears therefore that the criticisms of Adadurow and Didenko are based partly on an incorrect interpretation of their own data, and partly on an incorrect mechanism for the decomposition of methyl alcohol. On this basis they arrive at an alternative explanation of our experiments which is not in accord with the facts.

PHYSICAL CHEMISTRY LABORATORY
MCGILL UNIVERSITY, MONTREAL

RECEIVED JANUARY 21, 1936

COMMUNICATIONS TO THE EDITOR

THE PHOTOLYSIS OF ACETIC ACID

Sir:

In the course of a general investigation of the mechanism of the photolysis of acetic acid I applied the method of Paneth [*Ber.*, **62B**, 1335 (1929)] to the detection of free radicals. Using a light lead mirror followed in order by a heavy lead guard mirror and a light antimony mirror, approximately simultaneous disappearance of the two light mirrors was observed.

The efficacy of the guard mirror was checked by experiments with acetone. In a particular series of experiments, it was found that a guard mirror which was ineffective in preventing the removal of an antimony mirror in an acetic acid run was, after the lapse of a day, still effective in preventing such disappearance of a fresh antimony mirror in an acetone run, even though it itself was now visibly affected. The period of the latter run was equivalent (in free radical yield) to more than twice that of the acetic acid run. When, after the latter experiment, the guard mirror was reinforced by redeposition of lead, it was found that it was still ineffective in preventing the removal of the same antimony mirror in an immediately following run with acetic acid.

Except for the use of the guard mirror and the succeeding antimony mirror, the experiments bore a resemblance to those of Pearson [*J. Chem. Soc.*, 1718 (1934); *ibid.*, 1151 (1935)].

The effect on the lead mirrors may be attributed to the formation of free radicals, presumably methyl, and that on the antimony mirrors to the formation of atomic hydrogen in the photolysis of acetic acid in the vapor phase according to a mechanism

$$CH_3COOH + h\nu \longrightarrow CH_3 + COOH \quad (1)$$

$$COOH \longrightarrow CO_2 + H \quad (2)$$

Inasmuch as Farkas and Wansbrough Jones [*Z. physik. Chem.*, **B18,** 124 (1932)] offer good evidence [v. Franck and Rabinowitch, *Trans. Faraday Soc.*, **30,** 120 (1934)] for a primary formation of ultimate molecules according to the alternative mechanisms

$$CH_3COOH + h\nu \longrightarrow CH_4 + CO_2 \quad (3)$$

$$(CH_3COOH)_2 + h\nu \longrightarrow C_2H_6 + CO_2 + CO + H_2O \quad (4)$$

I am led to the conclusion that, in acetic acid, decomposition may occur either from a suitable constellation of atoms by rearrangement of bonds into equally stable constellations of other molecules or from a molecule of sufficient energy content into free radicals. The implications of this conclusion are being subjected to further test.

On the basis of the results of Pearson, Robinson and Stoddard, [*Proc. Roy. Soc.* (London), **A142,** 275 (1933)] the effect on the antimony mirror would have been unexpected since they report that the recombination of atomic hydrogen is catalyzed by a lead mirror. The results here indicate that at low concentrations of atomic hydrogen the recombination process is improbable. So far as known this is the first time that this method has been applied to the detection of hydrogen atoms in the presence of free radicals.

NEW YORK UNIVERSITY
UNIVERSITY HEIGHTS
NEW YORK CITY
MILTON BURTON

RECEIVED FEBRUARY 24, 1936

THE PHOTOCHEMICAL FORMATION OF ETHYLENE IODIDE IN SOLUTIONS OF CARBON TETRACHLORIDE

Sir:

Ethylene iodide, which decomposes photochemically when exposed to the 303 and 313 mμ mercury lines [This Journal, **57**, 2411 (1935)] and undergoes an iodine sensitized decomposition at wave lengths of 436 to 579 mμ [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 mμ 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 mμ (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 mμ 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)].

Department of Chemistry
University of Rochester
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Robert E. DeRight
Edwin O. Wiig

Received February 17, 1936

AN EXPLANATION OF THE RELATIVELY LARGE CONCENTRATION OF O^{18} 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

$$O_2^{16} + 2H_2O^{18}\,(l) = O_2^{18} + 2H_2O^{16}\,(l)$$

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 ± 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 surprising 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.

BYERLY LABORATORY
RADCLIFFE COLLEGE
CAMBRIDGE, MASSACHUSETTS
CHARLES H. GREENE
ROGER J. VOSKUYL

RECEIVED FEBRUARY 13, 1936

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]

$$U = e^{-a(r - r_{12})} - C'e^{-a'(r - r_e)}$$

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 $^1/_2\ kT$ 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.

THE JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND
MAURICE L. HUGGINS

RECEIVED FEBRUARY 24, 1936

β-ALANINE AND "BIOS"

Sir:

The recent discovery in our laboratory that synthetic β-alanine is highly potent as an agent for stimulating yeast growth has made it possible for the first time in history to grow yeast rapidly from a small seeding on a medium containing only well-recognized pure chemicals.

Investigations in the "bios" field may for our present discussion be placed in two groups: those in which a "sugar and salts" medium is basal, and those in which the basal medium also contains asparagin. Asparagin has been used in the senior author's laboratory because it was early recognized (1920) to be beneficial, and since it was likely to be present in extracts to be tested it was desired to eliminate the effects of all but the unknown factors. The use of asparagin media led to the discovery of "pantothenic acid," its universal occurrence and importance as a "growth substance" for protozoa and green plants as well as yeasts. The importance of pantothenic acid could not have been discovered in an asparagin-free medium because in such a medium pantothenic acid alone is relatively ineffective. On the other hand, the presence of asparagin in a medium (in the usual concentrations) masks the effect of at least one agent, *i. e.*, β-alanine, which is strikingly effective only in the absence of asparagin.

Some of the results obtained with β-alanine are shown in the accompanying table. The basal medium contained 5 mg. of inositol per liter in addition to sugar and salts. "Old process" yeast responded similarly to those listed except that vitamin B_1 is a necessary supplement. Pantothenic acid is also necessary for maximum growth.

YEAST CROPS

(MG. MOIST YEAST PER CULTURE)

Yeast	Control	1γ β-alanine added (to 12 cc. culture)	0.75 mg. aspartic acid added	1γ β-alanine and 0.75 mg. aspartic acid added
Wildiers	0.49	0.55	0.80	2.16
"Gebrüder Mayer"	.28	1.08	.28	1.62
W. Lash Miller	.32	0.92	.58	3.20
"Rasse M" (Kögl)	.42	1.74	.49	3.00

The importance of aspartic acid as a yeast nutrient (which is apparent from the results) is to be discussed in a separate paper from this Laboratory. It will be noted that the concentration of β-alanine used was only one part in 12 million parts of culture medium. At *very* high dilutions β-alanine may be slightly inhibitory, depending apparently upon the physiological state of the yeast. This in itself is not so remarkable because "growth substances" have previously been shown to be inhibitory under some conditions, but the small concentration which can be detected in this way is indeed striking. In a large number of tests we have observed a distinct inhibitory effect when 0.0001 γ was added to a 12-ml. culture. On this basis one gram of our synthetic material would be enough to dose detectably 120,000 tons of medium.

The discovery of the yeast stimulating action of β-alanine raises many interesting questions which are being investigated.

DEPARTMENT OF CHEMISTRY
OREGON STATE COLLEGE
CORVALLIS, OREGON
ROGER J. WILLIAMS
EWALD ROHRMAN

RECEIVED MARCH 23, 1936

NEW BOOKS

The Chemistry of the Synthetic Resins. By CARLETON ELLIS, Industrial Research Chemist. Reinhold Publishing Corporation, 330 West 42nd Street, New York, N. Y., 1935. Volumes I and II. 1615 pp. 15.5 × 23.5 cm. Price, $19.50.

The first edition of this valuable compilation appeared in 1923 under the title "Synthetic Resins and their Plastics." Since then the number of such products has increased by leaps and bounds, and is still gaining with steadily mounting velocity. Practically every issue of *Chemical Abstracts* records a long list of new ones. The need for such a new edition, therefore, was urgent and insistent, and the author has handled the enormous mass of pertinent literature in his usual masterly way. Even a hasty glance at the volumes, with their wealth of literature citations, graphic formulas, tables, charts and illustrations, will impress any one with the magnitude of the task and the painstaking care and thoroughness with which it has been carried out.

The author explains that the change of title does not indicate any change in the field covered, but is a recognition of our advancing knowledge of the causes and nature of resinification. This does not mean any neglect of plastics and plastic molding, for their status is likewise brought as fully up to date as is practicable in an undertaking of this size and scope. All subjects are handled from both their