calories. In 30% heavy water, however, the graph representing log k as a function of $1/T$ is an unbroken line throughout the entire temperature range with a value of E of 22,000 calories, similar to the constant for the rate in ordinary water at low temperatures (below 16°). The reduced rate of contraction and the interesting fact that the master reaction appearing only at low temperatures in ordinary water controls the rate over the entire temperature range in heavy water support the prediction of chemists that deuterium will have effects similar to those of low temperature. Assuming that the slowest master reaction of the catenary set controls the rate of water discharge from the vacuole, it appears that the catalyst in control at low temperatures in ordinary water is so slowed down in the heavy water that it governs the rate at all temperatures. The results should throw light on the chemical basis for the biological effect of heavy water and on the kinetics of the Arrhenius equation.

In green plant cells a new factor appears. Of 1088 cells of *Spirogyra* in 0.47% D_2O in the light of 60 foot candles, 72% were alive and healthy after two days but only 18% of 1129 cells survived in the dark. In ordinary water 32% of 1266 cells survived under the same light intensity and 16% of 789 cells in the dark. This suggests that heavy water in low concentration is favorable to photosynthesis. In fact, Reitz and Bonhoeffer [*Naturwiss.*, **22**, 744 (1934)] find that deuterium is taken directly into the carbohydrates of green algae. It is possible that the stronger bond between the heavy hydrogen and an adjacent atom, carbon, favors the production of a more stable intermediary product in photosynthesis (formaldehyde?) and also the C–C bonds may be strengthened slightly as in heavy acetylene.

We wish to express our thanks to Prof. L. L. Woodruff for helpful advice.

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RECEIVED JANUARY 24, 1935

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n-PROPYLARSONIC ACID FOR ZIRCONIUM

Sir:

In the January issue of THIS JOURNAL there appears an article entitled "*n*-Propylarsonic Acid as a Reagent for the Determination of Zirconium," by F. W. Arnold, Jr., and G. C. Chandlee, which is an abstract of Mr. Arnold's thesis.

Further study has shown that the directions, in so far as the separation of zirconium and tin is concerned, are inadequate.

STATE COLLEGE, PA. G. C. CHANDLEE

RECEIVED JANUARY 25, 1935

THE USE OF ARTIFICIAL RADIOACTIVE ELEMENTS AS INDICATORS IN CHEMICAL INVESTIGATIONS

Sir:

The use of the fruitful method of radioactive indicators introduced by G. v. Hevesy and F. Paneth has been limited to a very few heavy metals. The discovery of artificial radioelements by F. Joliot, I. Curie and E. Fermi extends this field to most of the common elements. The only, and surely temporary, limitation in their use is the small available activity, which necessitates the use of sensitive counters instead of the much simpler electroscope. The following experiment serves as an example of how the artificial radioelements can be put to use at the present time.

The problem was to determine whether or not the expected *exchange of bromine atoms* between *free bromine* and the bromine of *sodium bromide*, dissolved in water, takes place.

For this purpose 20.0 g. of sodium bromide was dissolved in 200 g. of water, placed in a 200-cc. round flask, surrounded by water (similarly to our experiment with silver) [A. V. Grosse and M. S. Agruss, *Phys. Rev.*, **47**, 91 (1935)] and bombarded for twenty-five hours with neutrons from a glass capsule placed in the center of the flask containing 100 millicuries of radon and 200 mg. of beryllium powder. After the irradiation the sodium bromide solution was divided into two equal parts: to the first 100 cc. containing 10.0 g. of sodium bromide, 24.0 g. of liquid bromine was added. Both solutions were evaporated in porcelain dishes on a boiling water-bath; the free bromine disappeared in the first solution after about half an hour. The sodium bromide obtained was dried at 150°. The activities of the two preparations were measured with a helium filled Geiger–Müller counter and a thyratron operated watch. The finely powdered preparations were evenly sieved on paper, coated with lacquer, then covered with very thin Japanese tissue paper, also coated with lacquer, and rolled into cylinders fitting the Geiger tube.

The weights of sodium bromide were about 2–4 g. and were determined by difference. Both preparations were measured for a thirty-hour period, beginning two hours after the end of irradiation; they both showed, after the first hour, an activity regularly decaying with a half period of about six hours, corresponding to E. Fermi's radiobromine [E. Fermi and co-workers, *Proc. Roy. Soc.* (London), **146,** 483 (1934)]. The other radiobromine, with a period of thirty minutes, as well as the sodium products, had mostly decayed in the first two hours. The activity of the *first* preparation, treated with bromine, *was 2.5 times smaller*, than the *second*, proving that an exchange of bromine atoms had taken place.

It is most probable that the exchange mechanism is described by the reactions

$$\begin{array}{ccc} NaBr \rightleftarrows Na^+ + Br^- \\ \updownarrow \\ Br_2 + H_2O \rightleftarrows Br^- + H^+ + HOBr \end{array}$$

If complete exchange has taken place, the ratio of activities should correspond to the mass ratio of free bromine to bromide bromine or equal 3.0:1. The observed deviation is surely due to the fact that part of the bromine has escaped the exchange mechanism, probably because the rate of evaporation was faster than the slow rate of hydrolysis [see W. C. Bray, THIS JOURNAL, **32,** 938 (1910); W. C. Bray and E. L. Connolly, *ibid.*, **33,** 1487 (1911); G. Jones and M. L. Hartmann, *Trans. Am. Electrochem. Soc.*, **30,** 295 (1917)]. This point shows that it also will be possible to measure, besides exchanges, reaction velocities and other phenomena.

The artificial radioelements will be of great value for the investigation of the mechanism of catalytic reactions. Especially radio-isotopes of carbon, nitrogen and oxygen (?) will, like the heavier stable isotopes of these elements, open, if available in sufficient quantity, an unlimited field of investigation in organic and biological chemistry.

Acknowledgments.—It is a pleasure to acknowledge our indebtedness to Dr. M. Cutler, of Michael Reese Hospital, and to Dr. H. Scott and Dr. E. Williams of Hines Veterans Hospital for the radon source, to Dr. W. D. Harkins for the loan of beryllium and to Mr. J. Allen, of the Physics Department, for his advice and help in building the counter. This work was partly supported by a grant from the Chemical Foundation.

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CATALYTIC EXCHANGE OF DEUTERIUM AND METHANE

Sir:

The researches of Hollings and Griffith [*Nature*, **129,** 834 (1932)] and of Turkevich, Howard and Taylor [THIS JOURNAL, **56,** 2254, 2259 (1934)] have shown, by adsorption measurements, that, on a variety of catalysts, activated adsorption of hydrocarbons may occur. The latter work shows that activated adsorption of ethylene occurs generally in a much lower range of temperature than that of the saturated hydrocarbons. Recent studies of Farkas, Farkas and Rideal [*Proc. Roy. Soc.* (London), **A146,** 630 (1934)] and of Horiuti, Ogden and Polanyi [*Trans. Faraday Soc.*, **30,** 663, 1164 (1934)] indicate that exchange between deuterium and unsaturated hydrocarbons can be achieved readily at surfaces of platinum, nickel and copper. These workers also show that the exchange with saturated hydrocarbons does not occur under conditions where the exchange with ethylene occurs rapidly. Using the technique developed in our earlier photochemical studies [THIS JOURNAL, **57,** 383 (1935)] we have examined the exchange, at reduced nickel catalyst surfaces, between deuterium and methane, choosing this latter as probably the most refractory and thermodynamically most stable of the hydrocarbons. By examining the infra-red absorption spectra of the products we have shown that deuterium and methane exchange to yield deutero-methanes in the temperature range 184–305°. At the upper temperature, equilibrium, which is on the heavy methane side, is established within twenty hours. At 218°, in the same time, the equilibrium position is not yet established, but, in fifty hours, equilibrium is obtained. The conversions are slower still at 184°. At 110° even in ninety hours no measurable formation of deutero-methane can be established. Curves of reaction velocity indicate very slow rates of exchange below 170°. We believe that this is evidence that the exchange reaction requires activated adsorption of methane, since other researches [Gould, Bleakney and Taylor, *J. Chem. Phys.*, **2,** 362 (1934)] indicate abundant activation of the deuterium at such surfaces under the given conditions. If our assumption is correct, the activated adsorption of methane is thus demonstrable at temperatures as low as 170°, which is at least 200 degrees lower than this is detectable by adsorption measurements. We assume that acti-