benzene was added and the material again boiled out *in vacuo*. This was done three times. The resulting colorless acid chloride was taken up in benzene and added to a benzene suspension of 12.3 g. of sodium *p*-nitrophenoxide. Considerable heat was evolved at the outset. The reaction was completed by boiling for two and one-half hours on the steam-bath. The mixture was then cooled, thoroughly extracted with water, aqueous sodium carbonate and water, dried over sodium sulfate and evaporated *in vacuo* at 95°. The crude phenolic ester, 15.5 g., yield 80%, was distilled in a Hickman molecular still at 0.001 mm. (bath 100°) taking two fractions, (A): α_D^{24} +1.51°, n_D^{25} 1.5106; (B) α_D^{24} +1.20°, n_D^{25} 1.5114. There was almost no residue. (A) and (B) were combined and redistilled in a Claisen flask yielding (C): b. p. (0.3 mm.) 128–135° (bath 176°), α_D^{23} +1.51°, d_4^{25} 1.1128, n_4^{25} 1.5109, and a residue (1 cc.) α_D^{23} +0.70°, n_D^{25} 1.5120. The former (C) was then separated into two fractions at 0.15 mm. (bath 160°), (E) b. p. 118–123°, $\alpha_D^{23.5}$ +1.52°, n_D^{25} 1.5114; (F) b. p. 124–125°, α_D^{23} +1.45°, $[M]_D^{25}$ +3.27°, $[M]_D^{25}$ max. +5.4°, d_4^{25} 1.1121, n_D^{25} 1.5113. Fractions (E) and (F) were light yellow and gave only a weak Beilstein test for halogen. The residue (0.5 cc.) was orange, dextrorotatory and gave a stronger Beilstein test for halogen.

Anal. (micro). Calcd. for $C_{13}H_{17}O_4N$: C, 62.12; H, 6.82; N, 5.58. Found: Fraction C: C, 62.00; H, 6.82; N, 5.52. Fraction F: C, 62.22; H, 6.66; N, 5.63.

Sodium *p*-Nitrophenoxide.—This salt was thrice recrystallized from water, dried at 120° *in vacuo* for twenty-four hours and allowed to cool *in vacuo* over phosphorus pentoxide. It was bright red and when hydrolyzed with dilute hydrochloric acid, formed *p*-nitrophenol, m. p. 110–112°.

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CONTRIBUTION NO. 109 PHILIP G. STEVENS

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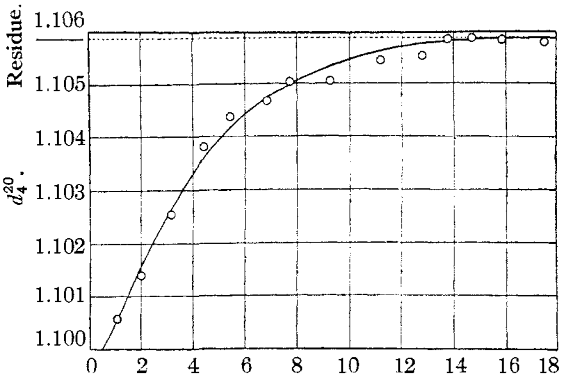
SOME PROPERTIES OF HEAVY WATER

Sir:

Experience gained in the production of comparatively large quantities of heavy water leads us to believe that the maximum density attainable by the electrolytic method is somewhat greater than that reported by Lewis and Macdonald [THIS JOURNAL, **55,** 3057 (1933)] for water containing less than 0.01% light hydrogen. Lewis and Luten [*ibid.*, **55,** 5061 (1933)] state the ratio of specific gravities of heavy and light waters at 25° to be 1.1056. We find d_{25}^{25} 1.1079. We also find the difference in refractive indices to be −0.00462 at 20° for the sodium D line.

Such water, of which we have prepared over 100 cc., has been subjected to prolonged electrolysis in order to determine whether any further increase in density takes place. For this purpose 25 cc. of maximum density water was placed in a carefully dried cell with 2% pure NaOD. The electrolytic gas was passed through a trap to remove spray and was ignited at a minute nozzle. The recovered water was not allowed to come into contact with the atmosphere. The density of the recovered water was taken at approximately 1-cc. intervals. The densities plotted against total weight recovered are shown in Fig. 1. Some time after constant density had been reached, the residual water in the cell was removed and repeatedly distilled. The density d_4^{20} was 1.1059. The fact that only 95% heavy water was obtained in the first 2 cc. illustrates the extreme readiness with which pure D_2O takes up moisture from the air and possibly from the glass walls of the apparatus. A cc. of water d_4^{20} 1.1038 was exposed to the atmosphere overnight and the density fell to 1.1016. Pure D_2O must be handled like any other anhydrous liquid.



Recovered water, g.

Fig. 1.—Density of recovered water in prolonged final electrolysis.

The ratio of the specific rates of discharge of light and heavy hydrogen at these high concentrations is about 6, which in view of the fairly large probable error cannot be considered as sensibly different from that obtaining throughout the more dilute stages of the process with either iron or nickel electrodes.

We find the freezing point of our maximum density water to be 3.82°, and the viscosity at 20°, 12.6 millipoises. An earlier report on the viscosity by Selwood and Frost [THIS JOURNAL, **55,** 4335 (1933)] was marred by an unfortunate error in calibration.

It may be of interest to add that prolonged fractional freezing of 90% D_2O has yielded no concentration. This is the result to be expected from the work of La Mer, Eichelberger and Urey [*ibid.*, **56,** 248 (1934)] on the freezing points of isotopic mixtures. Experience in the concentration of D_2O from tap water has shown that the ratio D_2O/H_2O in natural water is about 1 in 5 or 6 thousand, in agreement with the mass spectrographic study of Bleakney and Gould [*Phys. Rev.*, **41,** 265 (1933)].

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THE NATURAL SEPARATION OF THE ISOTOPES OF HYDROGEN

Sir:

The densities of water obtained from the Atlantic Ocean,[1] from the Dead Sea and the Great Salt Lake and from the hydrated mineral rasorite are greater than that of fresh water by several parts per million, thus indicating a natural isotopic fractionation of water presumably by distillation.[2] The discoveries of Lewis and of Taylor, Swingle, Eyring and Frost[3] of the inability of living organisms to live or to grow in deuterium oxide have suggested the possibility of a natural selection of protium in preference to deuterium in the animal and vegetable kingdom. On the other hand, dilute solutions of deuterium oxide seem to stimulate physiological activity,[4] a fact which would lead one to predict that deuterium could possibly be concentrated physiologically. Washburn and Smith[5] have found that in the case of a growing willow tree an isotopic fractionation of hydrogen in the direction of a preferential selection of deuterium does occur.

Before this interesting work of Washburn and Smith was known to me, I had begun an investigation of the relative abundance of deuterium in organic compounds by burning the compounds in air or oxygen, condensing the resulting water vapor and measuring the density of the water after purification. Kerosene from the Oklahoma oil fields and Mallinckrodt thiophene-free benzene obtained in the destructive distillation of coal were separately burnt at the surface of a sintered glass wick in an atmosphere of dried air until 600 cc. of water had been condensed in each case. After careful purification the water from kerosene had a density seven parts per million greater than that of ordinary water while the benzene water was about eight parts per million heavier. Water obtained from the combustion of honey was four parts per million heavier than that of ordinary water. These data are comparable to the results of Washburn and Smith, who found that water from the combined hydrogen in the willow tree was between five and six parts per million more dense than ordinary water. I hope to investigate natural products of an animal origin in the near future.

The data for kerosene may shed some light on the origin of petroleum.

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[1] E. S. Gilfillan, Jr., THIS JOURNAL, **56,** 406 (1934).

[2] Bur. Standards Tech. News Bull. 196, August, 1933.

[3] G. N. Lewis, THIS JOURNAL, **55,** 3503 (1933); H. S. Taylor, W. W. Swingle, Henry Eyring and A. A. Frost, *J. Chem. Physics*, **1,** 751 (1933).

[4] T. C. Barnes, THIS JOURNAL, **55,** 4332 (1933); *Am. J. Bot.*, **20,** 681 (1933); S. L. Meyer, *Science*, **79,** 210 (1934); O. W. Richards, *Am. J. Bot.*, **209,** 679 (1933).

[5] E. W. Washburn and E. R. Smith, *Science*, **79,** 188 (1934).

ACCELERATED DIFFUSION IN DYE SOLUTIONS

Sir:

In a recent paper [THIS JOURNAL, **56,** 52 (1934)], McBain and Dawson give striking illustrations of accelerated diffusion, of electrolytes in aqueous solution, through a porous glass membrane. We wish to draw attention to another type of accelerated diffusion which has recently been observed in this Laboratory. Our observations are for the free diffusion of azo dyes in the presence of electrolytes as determined by the Fürth [*Kolloid-Z.*, **41,** 300 (1927)] micro-diffusion method. This method is particularly adaptable to observation of effects arising from rapid motion of color ions, and gives results with an average experimental variation of less than 5%.

When an aqueous solution of the sodium salt of *p*-sulfobenzene-azo-benzene-azo-6-benzoylamino-1-naphthol-3-sulfonic acid and sodium chloride is allowed to stand for a month at 25°, the rate of diffusion of the color ion is markedly affected by the presence of sodium chloride in the solution into which diffusion occurs. The results are summarized in Table I.

Numerous attempts were made to carry out diffusion from dye solutions containing 1.0 g./l. of sodium chloride, into sodium chloride solutions varying from 0.75–1.0 g./l. concentration. In every instance, measurement of the diffusion constant proved impossible owing to an accel-