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)].

FRICK CHEMICAL LABORATORY HUGH S. TAYLOR
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PRINCETON, N. J.

RECEIVED MARCH 21, 1934

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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RECEIVED MARCH 21, 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-

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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).

TABLE I

VARIABLE DIFFUSION OF *p*-SULFOBENZENE-AZO-BENZENE-AZO-6-BENZOYLAMINO-1-NAPHTHOL-3-SULFONIC ACID (SODIUM SALT)

Solution (g./l.) of Dye	+ NaCl	Age of dye solution	Diffusing into NaCl solution, g./l.	*T*, °C.	$D \times 10^{-6}$ sq. cm./sec.
1.0	1.0	90 hours	...	27	2.39
1.0	1.0	90 hours	0.5	27	2.47
1.0	1.0	90 hours	.75	27	Not measurable
1.0	1.0	4 weeks	...	29	2.14
1.0	1.0	4 weeks	.5	30	3.03
0.5	1.0	48 hours	...	29	3.13
.5	1.0	48 hours	.5	30	3.22
.5	1.0	3.5 weeks	...	25	2.12
.5	1.0	3.5 weeks	.5	26	3.18
.5	1.0	3.5 weeks	.125	25	2.58
After addition of 1.0 g./l. NaCl to preceding dye solution					
0.5	2.0		...	26	2.20
.5	2.0		1.0	26	2.08

erated diffusion which produced a marked distortion of the color boundary within two to three minutes. The distortion is best described as the formation of small spearheads of color projecting for a distance of 0.5–1.0 mm. into the salt solution. This breaking of the color boundary may result in diffusion of dye throughout the entire cell chamber within a few minutes.

Possibility that the accelerated diffusion is produced by density differences in the two solutions is ruled out by the fact that the more dense solution is in the lower part of the cell. It was shown in a number of tests that, when the solution in the upper half of the cell is of the greater density, a turbulent mixing occurs in which the dye is partially displaced from its original compartment within a few seconds. On reversing the positions of the solutions the diffusion occurs as originally described.

Measured increases of 20–50% in the diffusion constant of aged dye solutions into dilute sodium chloride solutions, as compared with diffusion into water, are given in Table I. The diffusion rate into more concentrated salt solutions is increased several fold. The motion of the color ions in the aged dye solution is markedly affected by the presence of sodium chloride in the solution into which diffusion occurs at a concentration as low as 0.125 g./l. With a fresh dye solution no effect on the motion of the color ions is observed until this concentration of sodium chloride is approximately 0.75 g./l. This difference in the sensitivity of the color ions toward salt indicates that, in the aged solution, the dye has adsorbed a large portion of the electrolyte originally added. This marked affinity for electrolytes may account for the accelerated diffusion observed in these experiments.

These observations were made in the course of another investigation, and since further study of the phenomena reported cannot be made by the authors, this brief report is given to draw attention to additional instances of accelerated diffusion.

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SAMUEL LENHER
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RECEIVED MARCH 22, 1934

THE VAPOR PRESSURE OF MIXTURES OF LIGHT AND HEAVY HYDROGEN

Sir:

Although our apparatus was not designed for the purpose, and the amount of gas available was insufficient for accurate work, we have made some preliminary study of the vapor pressures of various mixtures of H^2_2 and H^1_2. These mixtures approximate closely to Raoult's law, as shown in Fig. 1, where the total vapor pressure is plotted against the mole fraction of H^2_2 at 18.65°K.

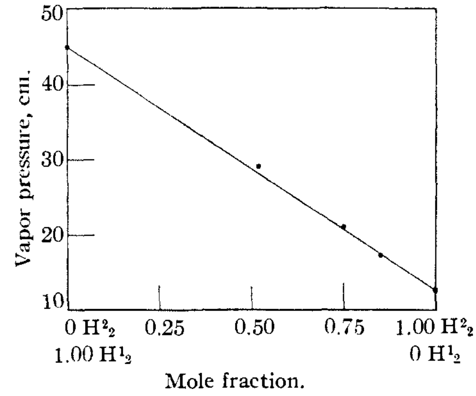

Fig. 1.

The temperature at which freezing begins also proved to be nearly linear with the mole fraction, as shown in Fig. 2, where the ordinate represents the temperature at which the first discontinuity in the vapor pressure curve occurs. In some cases a second discontinuity appeared, showing the final disappearance of the liquid phase. These observations indicate that while the solid phase contains a larger fraction of H^2_2 than the liquid phase, the difference is not great. We estimate